THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

STUDIES ON THE ELECTROCHEMISTRY OF CARBON AND CHEMICALLY MODIFIED CARBON ELECTRODES

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

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Norman, Oklahoma

1965

STUDIES ON THE ELECTROCHEMISTRY OF CARBON AND CHEMICALLY MODIFIED CARBON ELECTRODES

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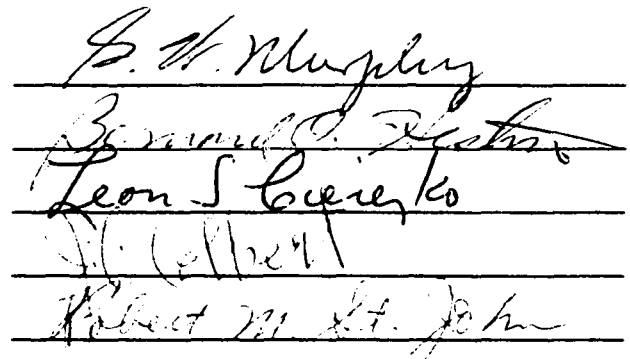

DISSERTATION COMMITTEE

ACKNOWLEDGEMENT

The author wishes to express his sincere gratitude to Dr. G. W. Murphy for suggesting this problem and for the advice he has given during the course of the research and the writing of this dissertation.

He is also grateful to the United States Department of the Interior for providing the funds for conducting the research.

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STUDIES OF THE ELECTROCHEMISTRY OF CARBON AND CHEMICALLY-MODIFIED CARBON ELECTRODES

CHAPTER I

INTRODUCTION

The potentials of carbon electrodes in aqueous solution are determined by the nature of the chemical groups forming the partly-oxidized surface, by impurities, and by electrochemically-active additives. The word carbon is used here as a general term and includes such substances as graphites, carbon blacks, and charcoals. As part of the development of an electrochemical water demineralization process, a systematic study of carbon electrode behavior has been undertaken.

It is convenient to classify electrodes according to their ion responsiveness; that is, their reversibility to one general ion type, either cation or anion, whether complete or not. An electrode giving the general half-cell reaction

$$ACl + e = A + Cl^- \qquad (1)$$

where A represents the nonconsumable electrode material, would be classified as anion-responsive. The well known

silver-silver chloride electrode is an example of anion-responsiveness. Similarly, representing the material of a cation-responsive electrode as C, we may write its half-cell reaction as

$$CNa = C + Na^+ + e \qquad (2)$$

A third type of responsiveness is possible; if an electrode were composed of a mixture of both A and C it would be capable of undergoing both of the above reactions and would be classified as cation-anion responsive. One type of responsiveness might far outweigh the other, depending on the relative amounts of the two materials present.

Implementation of the classification scheme calls for a rapid means of electrode characterization. With reversible electrodes of known properties, a concentration cell method has been employed to establish selectivity coefficients (as transference numbers) of ion-selective membranes. The basic theory of this method and a theory of ion-selective membrane permeability were developed independently by Teorell[1] and by Meyer and Sievers.[2] Many applications by later workers have been reported.[3,4] The method may be illustrated by considering the cell

$$Ag,AgCl/NaCl(a_1)/C_M/NaCl(a_2)/Ag,AgCl \qquad (3)$$

where C_M represents a cation selective membrane and a_1 and a_2 represent the activities of the two sodium chloride

solutions. This is a cell with transference[5] whose potential is

$$E = t_+(2RT/F) \ln (a_1/a_2) \qquad (4)$$

where t_+ is the transference number of sodium ion through the membrane, R is the gas constant in joules degrees^{-1} moles^{-1}, T is temperature in degrees Kelvin, and F is Faraday's constant. Employing the usual sign convention,[6] the potential would be taken as positive if a_1 is greater than a_2 (see Appendix II). In general, the potential of a concentration cell is

$$E = \pm t_{\pm}(2RT/F) \ln (a_1/a_2) \quad (a_1 > a_2) \qquad (5)$$

where $t_{\pm}$ is the membrane selectivity coefficient of the ion to which the electrodes are not reversible.

The selectivity of available commercial membranes is almost perfect at sufficiently low salt concentrations. The method therefore could be inverted to establish electrode responsiveness. With a perfect cation-selective membrane the concentration cell potential would be zero with cation-responsive electrodes and $2(RT/F) \ln (a_1/a_2)$ with anion-responsive electrodes, thus giving a clear cut distinction between the two types. Cation-anion electrodes would be expected to develop intermediate potentials between these extremes. The behavior of cation-anion electrodes is considerably more complicated than those with a single type of

responsiveness and will be considered in detail later.

The concentration cell method was applied to electrodes prepared from a commercial dispersion of graphite called Aquadag[7] (Acheson Colloids Co.). In this study the reliability of the method could not be established because of drifting potentials, but the conclusion was reached that the electrodes were cation-responsive.

Another important factor in the evaluation of an electrode is its capacity for the ion or ions to which it is responsive; that is, the amount of electrochemically active material capable of undergoing reaction 1 or 2 that it contains. Several types of demineralization cells designed to remove salt from water with the passage of current at appropriate applied potentials have been used to determine the capacity and responsiveness of carbon electrodes. Lyon[8] studied electrodes prepared from Aquadag in a demineralization cell consisting of two similar electrodes separated by an ion-selective membrane. He reported that the electrodes were cation-responsive.

Blair[9] improved the demineralization cell design using a cell composed of two electrodes, one cation-responsive and one anion-responsive. Silver-silver chloride electrodes were utilized as a standard of known properties. A large number of electrodes prepared from several different types of carbons and dispersing agents were studied. The results of this work indicated that most carbons are predominantly

cation-responsive without any prior chemical treatment, although the possibility of cation-anion responsive character with cation-responsiveness predominating could not be ruled out. Certain chemical treatments such as partial surface oxidation were found to increase cation capacity. No anion-responsive electrodes based on carbon were found with sufficiently high capacities to be practical in a demineralization process. While the demineralization cell method proved an effective means of electrode characterization, it is rather laborious and time consuming when the only information required is whether the electrodes are cation or anion responsive.

The objectives of this research are to establish the concentration cell method as a reliable means of electrode characterization, to study the factors influencing the responsiveness and capacity of carbon electrodes, to prepare a practical anion-responsive electrode based on carbon, to develop a theory of the potentials developed by cation-anion responsive electrodes, and to interpret the behavior of carbon electrodes in light of this theory.

Several articles have been published[27,32,33] by coworkers since the beginning of this study, based in part on the early results of this work. The findings of these subsequent studies also help to clarify or confirm some of the results which will be reported here. References will be made to these at the appropriate places.

CHAPTER II

PRINCIPLES

The Nature of Carbon

The term carbon includes a number of substances with widely varying properties. Carbons are usually classified by their method of preparation or the materials from which they were formed. Three general types are usually distinguished: graphites, carbon blacks, and charcoals or chars. There are several subdivisions within each of these classes, such as channel blacks, acetylene blacks, sugar chars, etc.

Despite a profusion of literature on the subject, knowledge of the exact nature of carbon is far from complete, and there is much conflicting evidence. One of the major difficulties has been that of obtaining well defined substances. There are many similarities between the different types of carbon, and present knowledge offers considerable insight into the ion-responsive behavior of carbon electrodes.

Crystal structure. The graphite crystal consists of layers of carbon atoms held together by weak van der Waals forces.[10,11] The atoms in the layers are arranged in hexagonal rings, each atom sharing its four electrons with three

of its neighbors and resonance imparting about 1/3 double bond character to each carbon to carbon bond. These resonating electrons account for the electrical conductivity of graphite. Each layer may be regarded as a combination of benzene rings although the structure is more quinone-like than aromatic.[11]

Riley[12] has shown that chars prepared from carbohydrates are composed of crystallites having a graphite structure. The size of the crystallites increases with the temperature of carbonization.

Studebaker[13] characterizes carbon blacks as having a graphite structure which is not quite regular, similar to that of chars. These crystallites contain strained bond angles, hydrogens on the edge carbon atoms and edge carbon atoms with incompletely filled valencies. Garten and Weiss[14] also propose these carbons with unshared electrons, stabilized by resonance, which they call free radicals. Studebaker states that the presence of edge hydrogen atoms lends a certain aromatic character to the carbon lattice.

Graphite compounds. Many interstitial compounds of graphite have been prepared and characterized. This subject has been thoroughly reviewed by Riley.[11] The possibility that the ion-responsiveness of graphite electrodes could be accounted for by the formation of this type of compound has been investigated.[7] In this study the conclusion was reached that interstitial graphite compounds were not important in

determining carbon electrode behavior.

Carbon-oxygen surface complexes. Carbons have been found to contain surface oxygen complexes. The type and amount of these complexes depends on the method of preparation and any subsequent treatment such as activation or chemical oxidation.[13] These complexes have been found to be important in determining the adsorptive, catalytic, and electrical properties of carbon.[15] In recent years great strides[13-18] have been made in identifying these complexes as organic functional groups and in understanding the relationships between these groups and many carbon reactions. There is some disagreement as to which groups are present or predominate on the carbon surface; but the most commonly mentioned are phenolic hydroxyl, (or hydroquinone), quinone, carboxylic acid, ketone, lactones of both normal and fluorescein types, chromene, and the free radical groups which were mentioned above.

Adsorption of electrolytes by carbon. It was observed by Kolthoff[19] and King[20] that sugar chars adsorb acid and alkali differently according to the temperature of activation. This has been the subject of much study, and several conflicting theories advanced have been critically reviewed by Steenberg[21] and Hassler.[22] Recently Garten and Weiss have successfully interpreted this phenomenon in terms of several of the organic functional groups mentioned above.[14,16,17]

Ion Responsive Behavior of Carbon

The ion responsive behavior of carbon electrodes can be satisfactorily explained in terms of surface oxygen complexes. Several of these complexes are capable of existing in two oxidation states, one of which is charged, and therefore acts as an ion-exchanger.

The quinone and hydroquinone groups proposed by Garten and Weiss[14] could, in sodium chloride solution, undergo the half-cell reaction

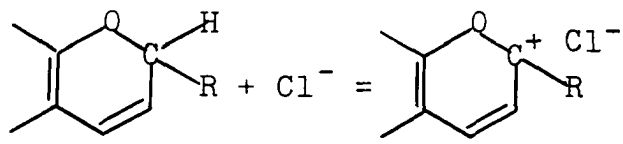
$$\text{C=O} + Na^+ + e = \text{C-O}^-Na^+ \qquad (6)$$

where C represents an edge carbon atom in the lattice. This quinone-hydroquinone couple is cation-responsive.

Oxidation-reduction reactions involving edge carbon atoms with unfilled valencies (free radical groups)[13,14] would give anion-responsiveness according to the equation

$$\text{C}\cdot + Cl^- = \text{C}^+Cl^- + e \qquad (7)$$

while the chromene-carbonium ion couple proposed by Garten and Weiss[16] would be cation-anion responsive:



(8)

Other groups such as carboxylic acid would be charged and ion-exchangers but would not be expected to undergo redox

reactions. These groups, however, could yield cation-responsiveness by controlling the amount of specifically adsorbed ions.

It should be borne in mind that any of the surface oxygen complexes could be hydrolyzed to some extent. However, it is assumed that in neutral solutions with relatively large amounts of sodium and chloride ions present, the above reactions would predominate.

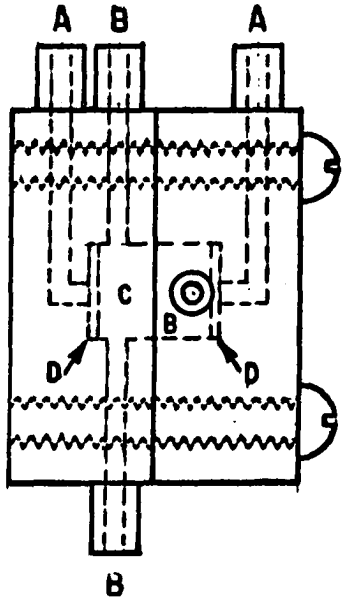
CHAPTER III

EXPERIMENTAL

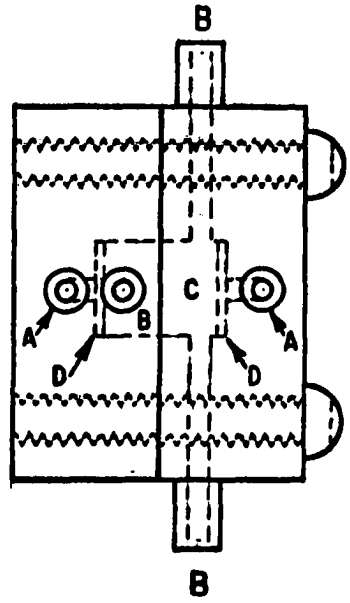
Development of Concentration Cell Method

The initial experiments in this area were carried out in the same cell that was used in previous work.[7] This cell, which will be designated concentration cell one (CC-1), is illustrated in Figure 1. It was made from two Lucite plates 2 x 2 x 3/4 inches and held together by 4 bolts. The Lucite plates each have cylindrical chambers, 1/2 inch in diameter by 3/8 inch deep, which hold the electrode being tested. Electrical contact was obtained with the electrodes through platinum discs at the bottom of each chamber which were cemented to the Lucite with Epibond Resin #121 (Furane Plastics, Inc., Los Angeles, Calif.) to give a liquid tight seal. The holes marked A in the figure were filled with mercury which made contact with the back of the platinum plates. In later experiments the platinum discs were replaced with wires sealed into the mercury tubes with Epibond #121. Solutions were introduced into the electrode chamber through the tube marked B.

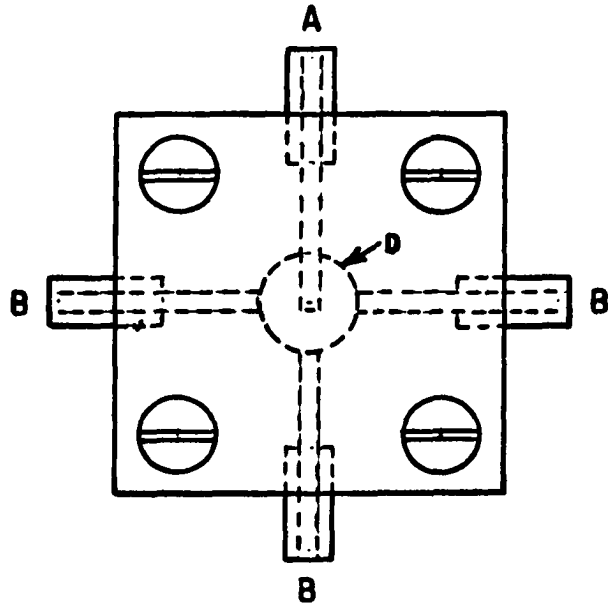
Because of the long term potential drifts a Sargent



a - SIDE VIEW



b - TOP VIEW



c - FRONT VIEW

FIGURE 1

CONCENTRATION CELL - 1 (CC - 1) ACTUAL SIZE

A - MERCURY CONTACT TUBES
B - INLET AND OUTLET TUBES
C - ELECTRODE CHAMBER
D - PLATINUM DISC

Strip Chart Recorder, Catalog No. S-72150 (E. H. Sargent Co., Chicago, Ill.) was used to record potentials for all concentration cell experiments. Over the experimental range the instrument recorded to the nearest millivolt and could be estimated to a tenth of a millivolt with $\pm$0.1 percent accuracy.

The electrolyte solutions were 0.1 N or 0.01 N sodium chloride. Concentrations were determined by comparing the conductance of the solutions with a standard curve of conductance vs concentration of sodium chloride. Conductance measurements were made with an Industrial Instruments Co. Bridge, Model RC.

The first attempts at eliminating potential drifts were concentrated on improving the control of variables such as temperature, solution concentration, flow rate, etc. The electrodes used in this series were prepared from Aquadag (Acheson Colloids Corp., Port Huron, Michigan), which is an aqueous dispersion of graphite containing 22 percent solids. The Aquadag was diluted with an equal volume of water and a patch made from Dacron felt (Troytuf felt of Dacron, Troy Blanket Mills, New York, N. Y.) was soaked in this mixture. After air drying, the patch was oven dried for several hours at 110°C. This type of electrode had been studied in demineralization cells[8,9] and found to be cation-responsive. Membranes used were Nalfilm 1 (cation-permeable) and Nalfilm 2 (anion permeable) manufactured by Nalco Inc., Chicago, Ill.

Experimental Procedure

The electrodes were cut from the large patch with a cork borer of the proper size to fit into the electrode chambers. Three or four discs were placed in each compartment. The two compartments were separated by a membrane and the gasketing surface was made leak-tight with stopcock grease. The cell was kept in a constant temperature water bath maintained at 25 ± 0.1°C. Tenth normal sodium chloride solution was introduced in one compartment and hundredth normal solution in the other. The solutions were gravity fed into the cell and were kept flowing throughout the course of an experiment. The solutions were stored in five gallon bottles about seven feet above the cell so that changes in fluid level were small compared to the total hydrostatic head. Flow rate was controlled by stopcocks in the line; it could be maintained at a reasonably constant value throughout the course of an experiment. The level of the effluent tubes was maintained slightly higher than the cell in order to keep a small positive pressure and thereby eliminate the possibility of bath water leaking into the cell. Effluent concentrations were checked periodically by conductance measurements. It was found that the solutions did not change concentration while passing through the cell. The potential was recorded continuously during each experiment.

A large number of experiments were carried out in this manner. Many changes in techniques and instrumentation

were tried in order to eliminate the potential drifts. These experiments will not be discussed because they were unsuccessful.

Two blank experiments, however, are worth mentioning. Both of these experiments were conducted with both compartments filled with 0.1 N NaCl solution and an anion-exchange membrane. The cell contained freshly prepared Aquadag electrodes during experiment CC-1-22. (The experiment code designations are discussed in Appendix I.) The Aquadag electrodes were removed for experiment CC-1-27 and only the platinum discs were in contact with the solution. The cell potentials were about the same in both experiments, as can be seen in Figure 2. Two other similar experiments without the membrane in the cell gave similar results.

To determine if the platinum contacts were responsible for the potential drifts, two platinum wires were made into loops, connected by lead wires to the recorder, and immersed in a beaker of 0.1 N NaCl solution. The variation of potential with time under these conditions is shown in Figure 3, Curve 1. Curve 4 of Figure 3 shows the result of adding an equimolar mixture of ferric chloride and ferrous sulfate to the sodium chloride solution; the potential dropped to zero and remained there for the duration of the experiment. This led to the conclusion that the potential between two platinum electrodes is meaningless in the absence of a clear-cut oxidation-reduction reaction at the electrode

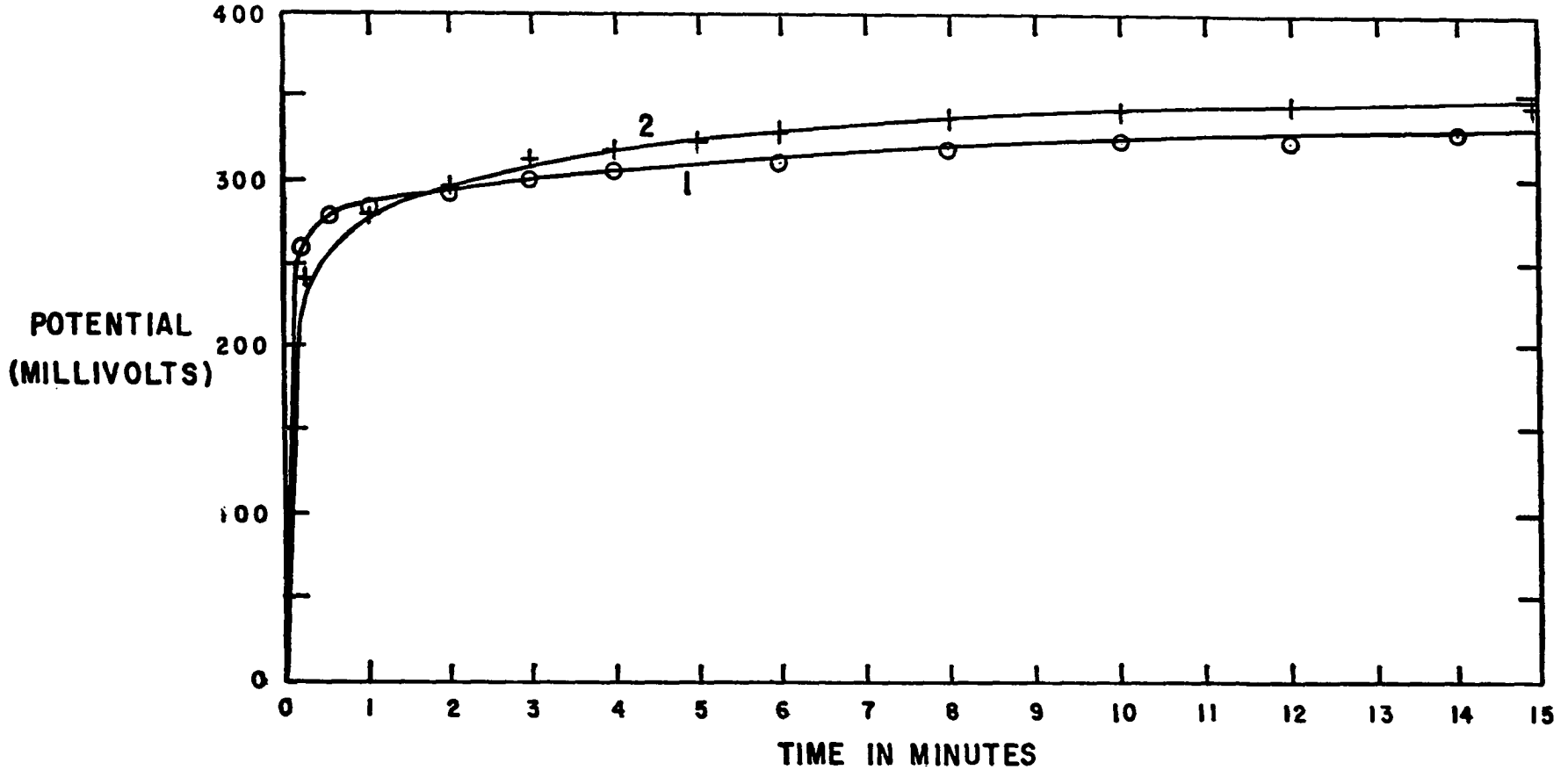


FIGURE 2

CONCENTRATION CELL EXPERIMENTS CCI-22 AND CCI-27
ANION-SELECTIVE MEMBRANE, 0.1 N NaCl SOLUTION, BOTH SIDES OF CELL

1 - EXPERIMENT CCI-22 (PT,G/A/G,PT) WITH GRAPHITE ELECTRODES
2- EXPERIMENT CCI-27 (PT/A/PT) WITH BRIGHT PLATINUM CONTACTS ONLY

surfaces. The results of two other experiments with Aquadag electrodes in contact with the platinum wire in 0.1 N NaCl solution are shown by Curves 2 and 3 in Figure 3. Curve 2 was obtained with freshly prepared electrodes while Curve 3 was obtained with electrodes which had been electrically preconditioned.

The conditioning treatment consisted of placing two electrode patches in 0.1 N NaCl solution and electrolyzing them for several hours. The applied potential was maintained between 0.8 and 0.9 volt, and the polarity was reversed every thirty minutes. After conditioning, one of the electrodes was cut in half, and the two halves were used in the experiment.

The resemblance between Curves 1 and 2, and between Curves 3 and 4 indicated that the electrodes were not electrochemically active; that is, they were not capable of undergoing clear-cut oxidation-reduction reactions when freshly prepared, but became activated by the conditioning process. Electrical preconditioning was therefore adopted as a routine procedure for concentration experiments.

Experiment CC-1-37. Freshly prepared Aquadag electrodes were conditioned in the manner described above. The electrode which was negative at the last reversal of polarity of the applied potential (the reduced electrode) was cut up and placed in the cell with an anion-selective membrane. Both electrode compartments were filled with 0.1 N NaCl. The

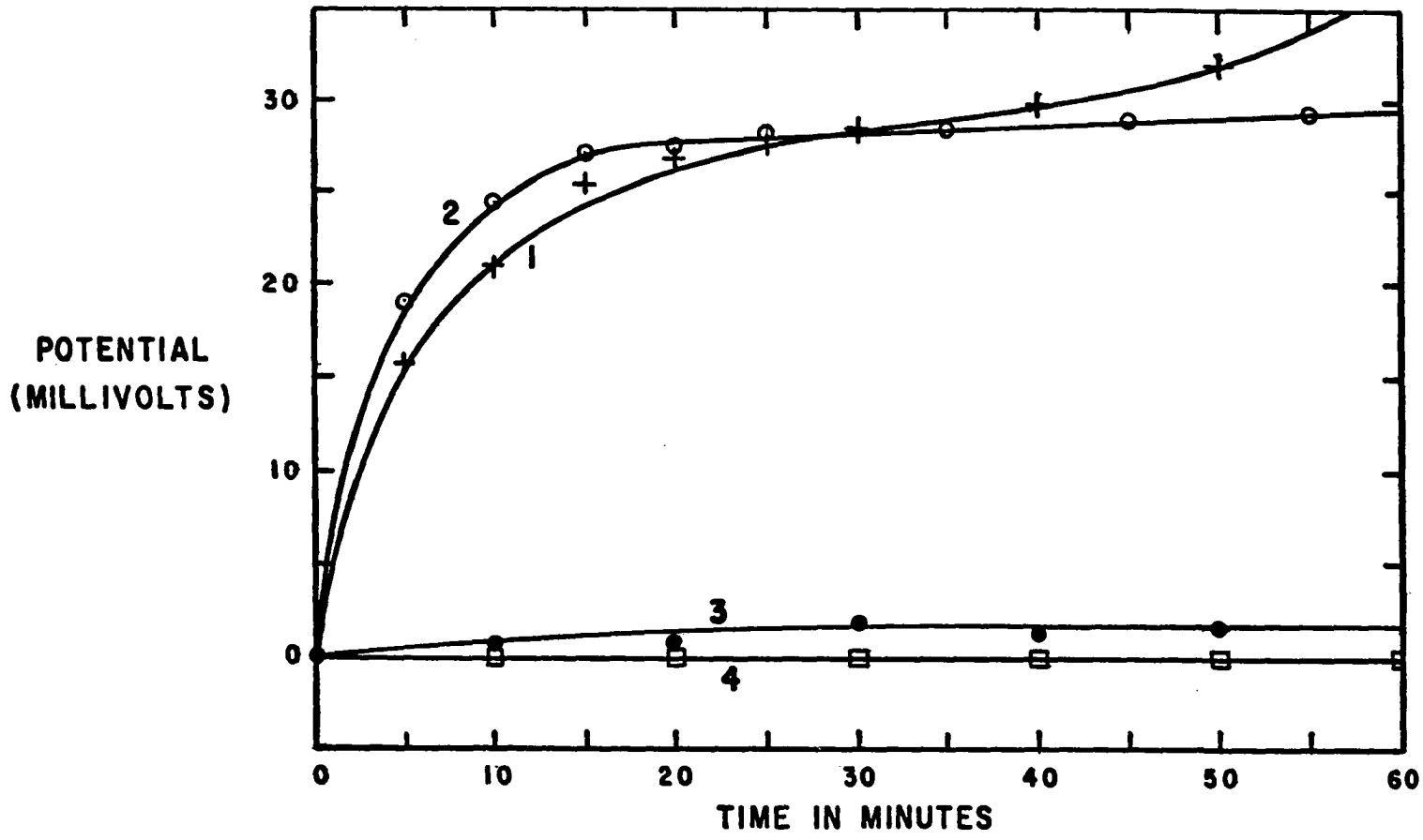


FIGURE 3

POTENTIALS DEVELOPED BY PLATINUM WIRE ELECTRODES ALONE AND IN CONTACT WITH OXIDATION-REDUCTION SYSTEMS

1 – PT WIRES IN 0.1 N NaCl

2 – PT-GRAPHITE (UNCONDITIONED) IN 0.1 N NaCl

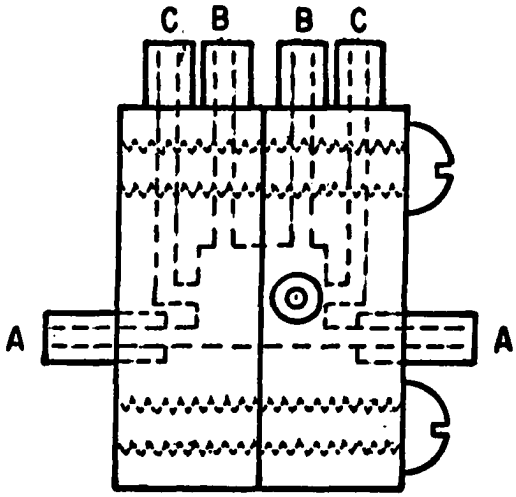
3 – PT-GRAPHITE (CONDITIONED) IN 0.1 N NaCl

4 – PT-IN 0.1 M NaCl + 0.1 M Fe^{++}, AND 0.1 M Fe^{+++}

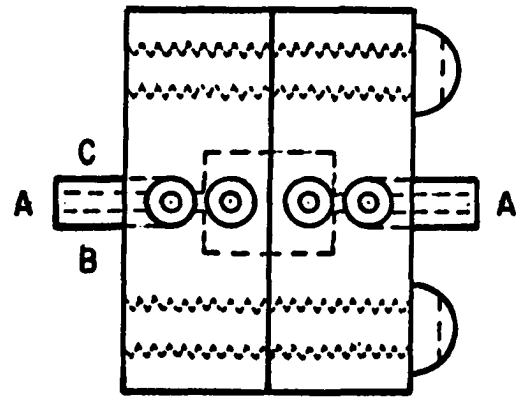
electrodes were shorted together until the potential remained within 2 millivolts of zero for several minutes after unshorting. The 0.01 N NaCl solution was introduced into one compartment. Potential rose slowly to -6 millivolts and then began changing at a slow but steady rate to -36 millivolts in 28 hours.

The slow response of potential indicated that the electrode in the chamber in which the 0.01 N NaCl solution was replacing the 0.1 N NaCl solution was not reaching concentration equilibrium rapidly enough. The electrodes were removed from the cell, marked so that they could be returned to the same chambers, and stored for future use. The cell was then modified as shown in Figure 4. The solution entry tubes, A, were plugged with Epibond resin, and new tubes, B, were drilled so that the entering solution was forced through the porous electrode material. This modified cell was designated as CC-1A.

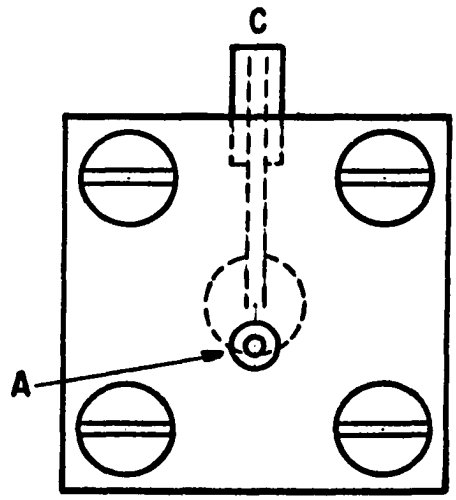
Experiment CC-1A-38. The electrodes from experiment CC-1-37 were used in this experiment with an anion membrane. The 0.1 N and 0.01 N NaCl solution were returned to the same compartment as in the previous experiment. The results are shown in Figure 5 in five distinct steps. The electrodes had the same potential at the beginning of step 1 as at the end of CC-1-37 and continued to drift in the same direction. The 0.01 N NaCl solution was replaced with 0.1 N NaCl solution in step 2, and a bias potential was measured. This bias was



a- SIDE VIEW



b- TOP VIEW



c- FRONT VIEW

FIGURE 4

CONCENTRATION CELL IA (CC IA ACTUAL SIZE)

apparently introduced by having the electrodes in contact with solutions of different concentrations. The electrodes were shorted together during step 3. The bias was thereby removed, as indicated by the zero potential obtained during step 4 with the cell unshorted. The 0.01 N NaCl solution was then introduced in step 5, and a potential of -106 millivolts was obtained before the slow downward drift set in.

If the potential of -63 millivolts obtained at the end of step 1 is corrected for the bias of +42 millivolts at the beginning of step 2, the value obtained is -105 millivolts. Thus the potential obtained at the start of the experiment when the solutions are changed from 0.1 N in both compartments to 0.1 N in one and 0.01 N in the other is gradually reduced by some process which is caused by the electrodes being in contact with solutions of different concentrations. The reasons for this drift will be considered later. However, this experiment showed that the bias could be corrected for and reproducible potentials could be obtained.

Membrane Selectivity Coefficients. The selectivity coefficients were determined in CC-1 using silver-silver chloride electrodes. The electrodes were prepared by electrolyzing silver wire mesh in 0.1 N sodium chloride solution. The results obtained with 0.1 N and 0.01 N sodium chloride solutions are summarized in Table 1.

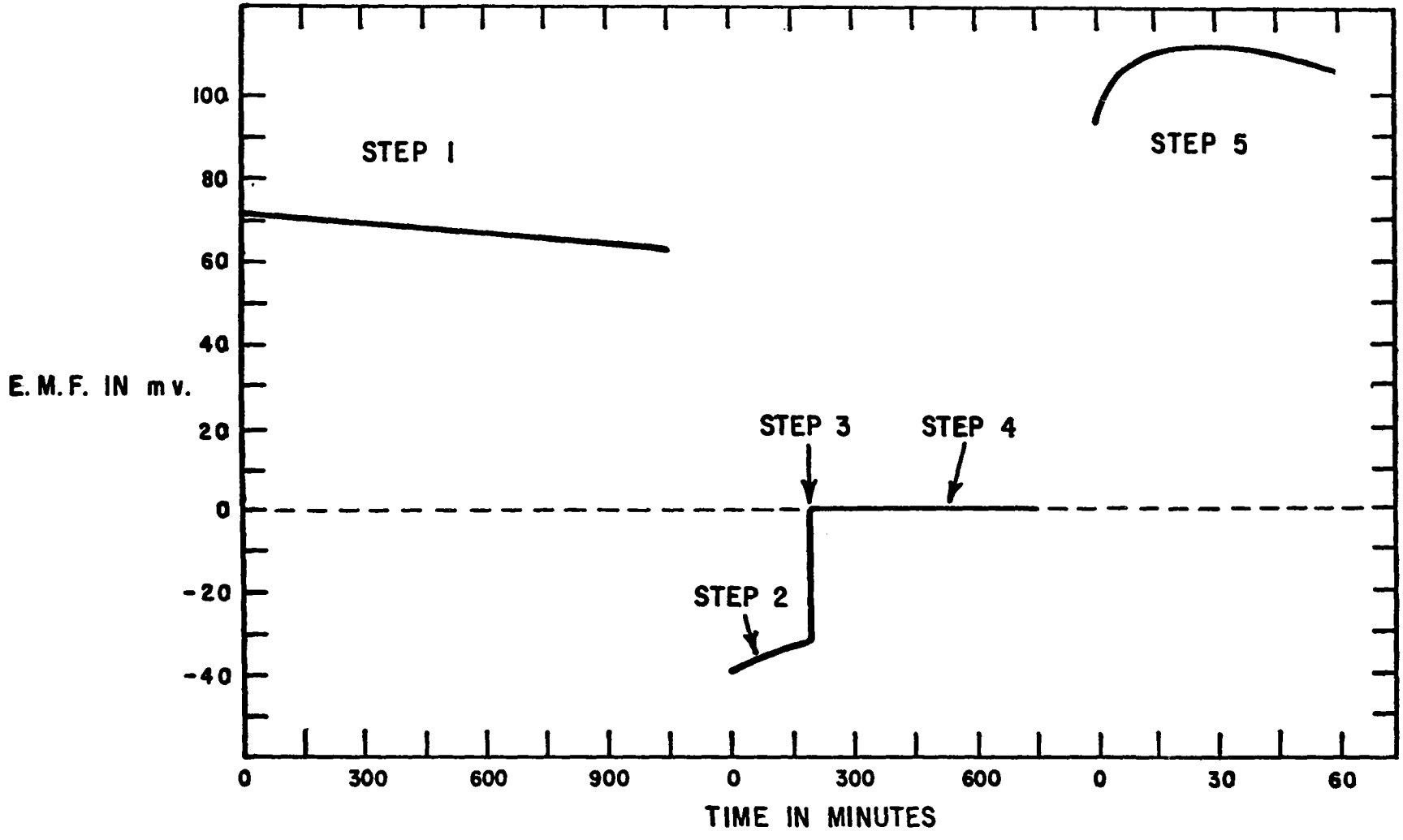


FIGURE 5

POTENTIAL DIFFERENCES FOUND IN CONCENTRATION CELL EXPERIMENT 38

TABLE 1

MEMBRANE SELECTIVITY COEFFICIENTS

Experiment No.	Membrane	Potential (mv)	t_+
CC-1A-44	Cation	-109.0	0.986
CC-1A-45	Anion	+ 1.2	0.011

Some potential drift was obtained in CC-1A-45. probably due to strains in the silver wire. The value reported represents an average of several trials.

The t_+ values were calculated with equation (5) using values of 0.778[28] for the activity coefficient of 0.1 N sodium chloride at 25°C and 0.903[29] for the activity coefficient of 0.01 N sodium chloride.

The concentration cell potentials that would be expected using these membranes with perfect electrodes, responsive to only one ion type, are summarized in Table 2.

TABLE 2

CONCENTRATION POTENTIALS FOR PERFECT ELECTRODES

Electrode Responsiveness	Membrane	Potential (mv)
Cation	Anion	-109.3
Cation	Cation	+ 1.6
Anion	Cation	+109.0
Anion	Anion	- 1.2

Characterization of Electrodes

Apparatus and Procedure

A new concentration cell was designed to make routine electrode characterization easier. This cell is illustrated in Figure 6. It consists of two Lucite plates 2 1/4 x 2 x 3/4 inches held together by four brass bolts. Each plate has an electrode chamber 3/4 x 1/2 x 1/2 inches accommodating two electrodes. The two chambers were separated by an ion-selective membrane. The positions of the four electrodes are indicated by the shaded areas.

Electrical contact was made by platinum wires in the four long tubes marked A, A', B, and B'. The wires were sealed in position with Epibond resin as in the case of CC-1. External contacting was made by soldering the wires to brass terminals which were cemented to the top of the tubes.

The solution entry tubes, C, were situated so that entering solutions had to pass through the porous electrodes and exit through the tubes marked D.

An automatic switching device and an electrically operated double pole double throw switch were added to the conditioning apparatus so that the conditioning operation could operate unattended. The circuit diagram of the conditioning and potential measuring circuit is shown in Figure 7.

A manifold consisting of three needle valves to control solution flow is illustrated in Figure 8.

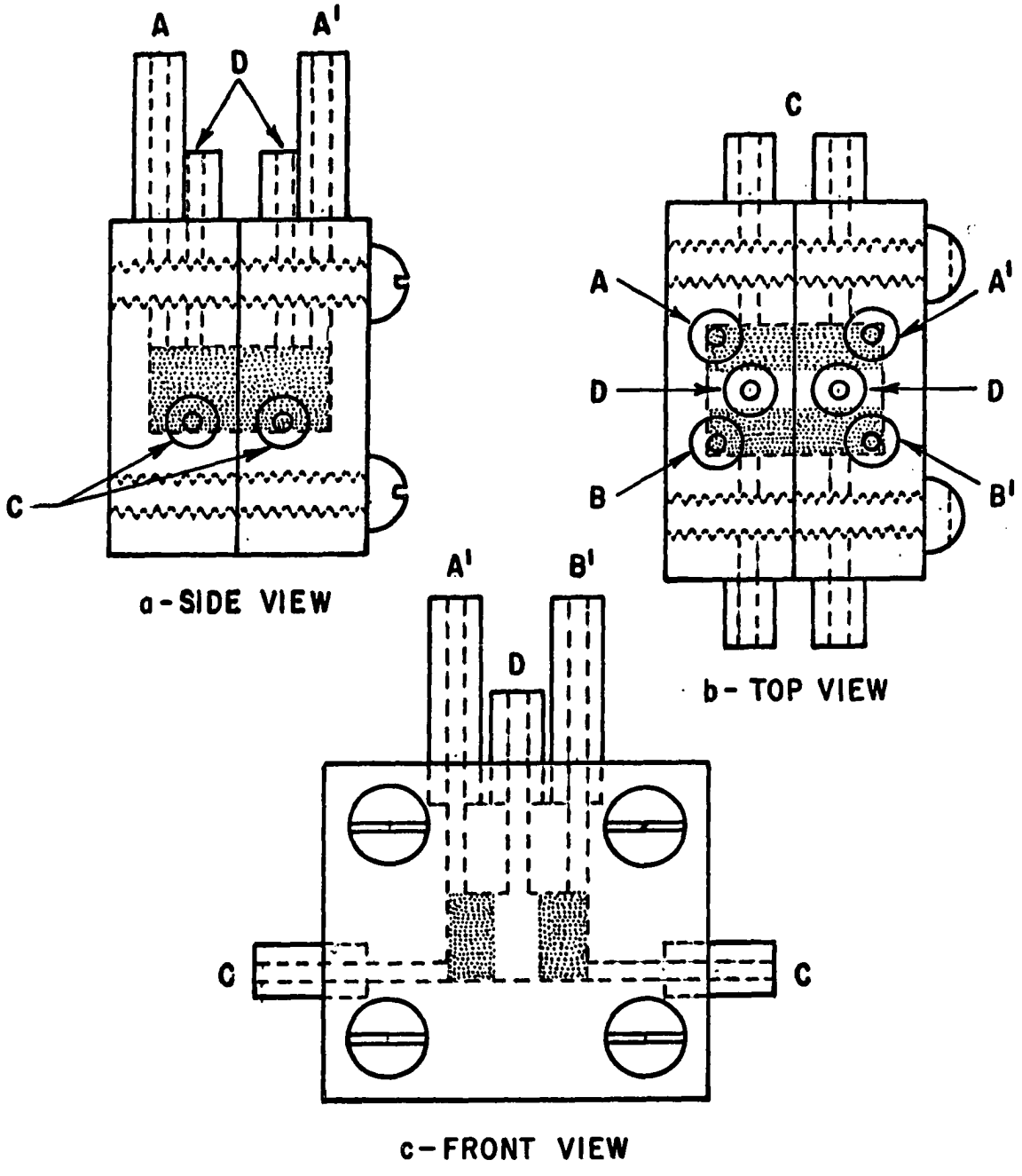


FIGURE 6

CONCENTRATION CELL 2 (CC 2 - ACTUAL SIZE)

A-B-A-B — ELECTRICAL CONTACT TUBES
C····· — SOLUTION ENTRY TUBES
D····· — SOLUTION EXIT TUBES

SHADED AREA - ELECTRODE POSITIONS

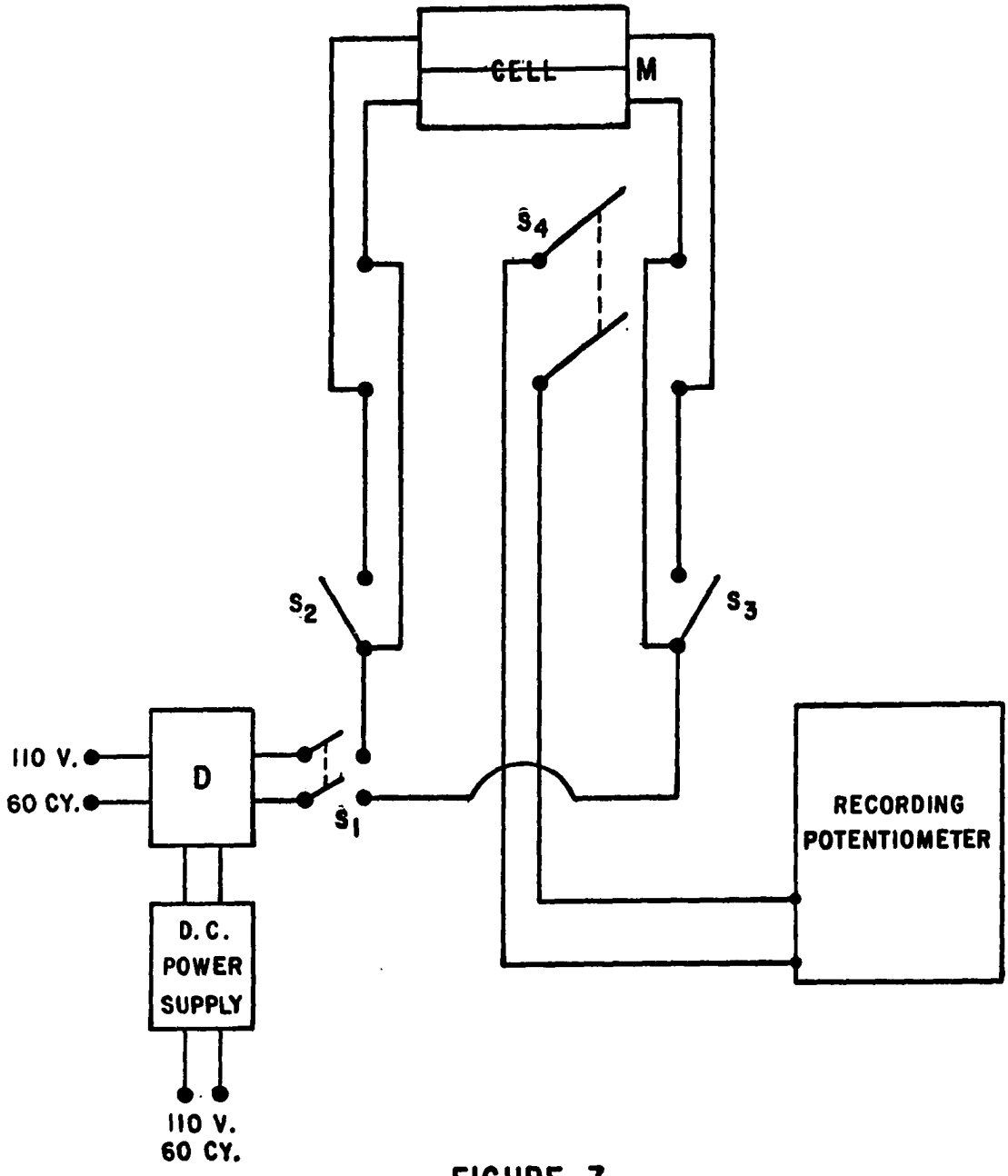


FIGURE 7

CIRCUIT FOR ELECTRODE CONDITIONING AND CONCENTRATION POTENTIAL MEASUREMENT

D - AUTOMATIC TIMER AND REVERSAL SWITCH
M - ION EXCHANGE MEMBRANE

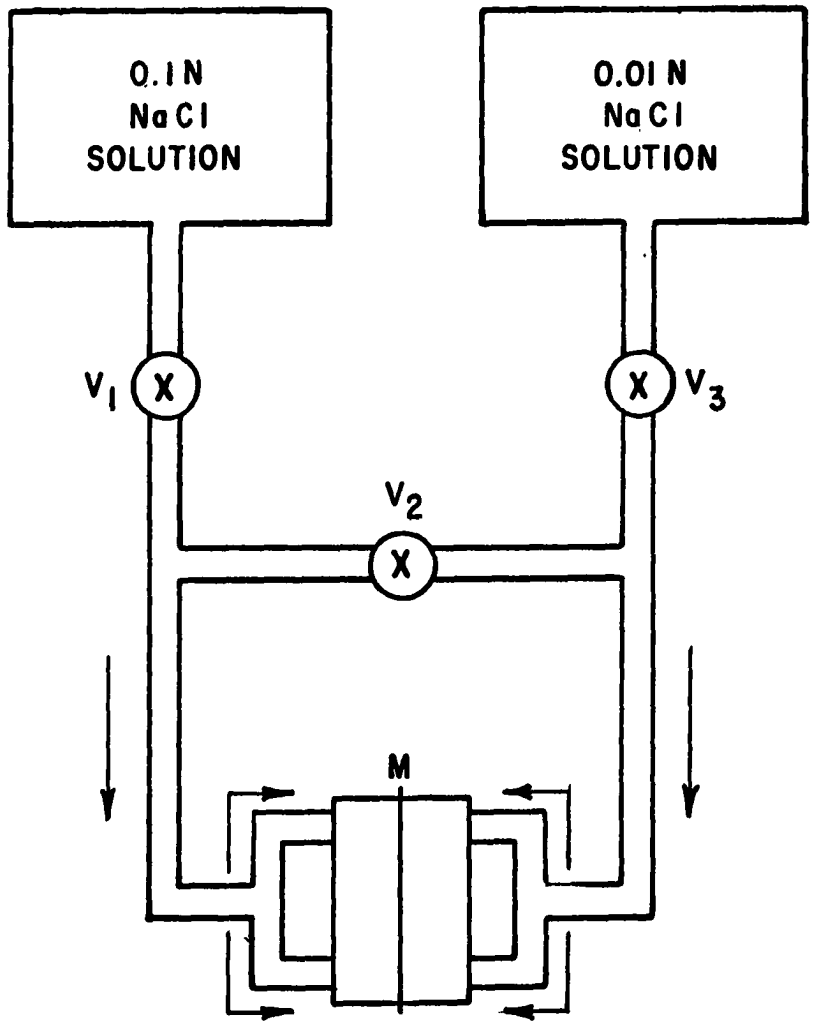


FIGURE 8

SCHEMATIC OF MANIFOLD TO CONTROL SOLUTION FLOW TO CC-2

M - ION-EXCHANGE MEMBRANE

After drying, the electrodes were cut into 1/2 inch squares. Four of these squares were placed in each of the four electrode positions and the void space filled with Dacron felt patches (1/2 inch squares). These porous patches were not impregnated with carbon. Their function was to keep the electrodes separated and reduce the solution volume within the cell. The cell was made leak tight with stopcock grease and assembled with an ion-selective membrane separating the two halves.

The procedure followed in conditioning the electrodes may best be explained by referring to Figures 7 and 8. At the beginning all switches were open and all valves were closed. The assembled cell was placed in the constant temperature bath with the wire and solution tubing attached to their proper places. Valves V1 and V2 were opened to fill both compartments with 0.1 N NaCl solution. The solution flow rate was adjusted to two or three drops per minute, and switches 1, 2, and 3 were closed connecting the electrodes to the conditioning power supply. The conditioning potentials varied from experiment to experiment between 0.4 to 0.8 volts, but was held constant for any given experiment. The direction of the conditioning potential was reversed every thirty minutes by the automatic switching device. The minimum conditioning time was one and one-half hours (3 half cycles). Sometimes conditioning lasted overnight.

The switch S1 was opened to end the conditioning

process. At this time the polarity of the electrodes during the last half-cycle was recorded. The pair of electrodes connected to the positive terminal of the power supply were designated as the oxidized pair and the other as the reduced pair. Switches S2 and S3 were left closed, shorting the electrodes by pairs. Thus one reduced electrode was shorted to the other reduced electrode and the oxidized to the oxidized. The time which the electrodes were left shorted varied from one hour to overnight. During this period the flow of 0.1 N solution through the cell continued at the same rate.

The electrodes were then unshorted by opening switches S2 and S3. The electrode pair to be tested was connected to the recorder by closing switch S4 to the proper position. If the potential remained within plus or minus five millivolts of zero for five minutes after unshorting, the bias was considered to be removed. If not, the shorting procedure was continued until this was accomplished. Then with switches S2 and S3 open and S4 closed, valve V2 was closed and valve V3 opened to introduce 0.01 N NaCl solution into one electrode chamber, thus causing a concentration difference across the membrane. Valve V3 was opened wide for about one minute to flush the 0.1 N NaCl solution from the chamber and then adjusted until the flow was about 3 drops per minute.

The results of a typical experiment are shown in Figure 9. Immediately after the concentration difference

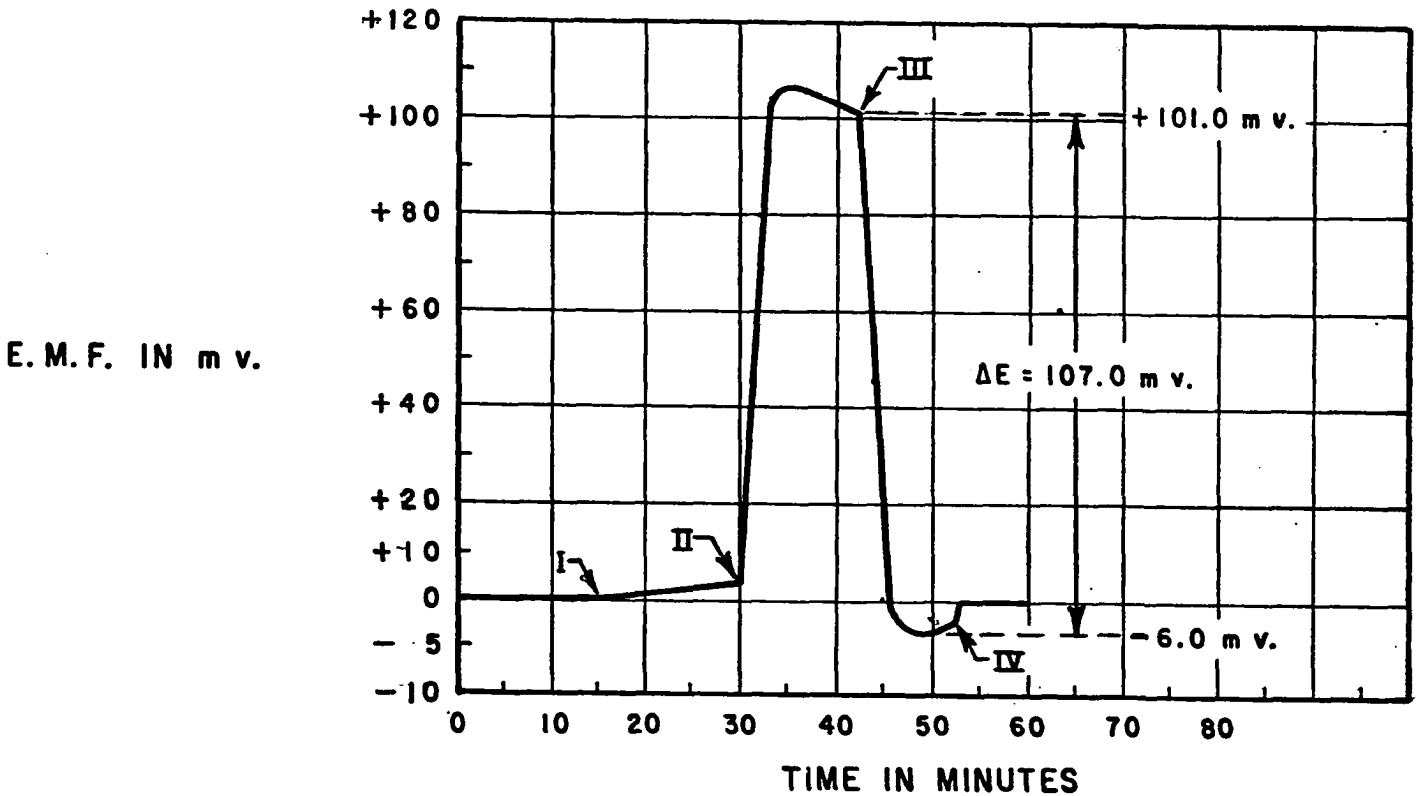


FIGURE 9

E.M.F. vs. TIME FOR A TYPICAL CONCENTRATION CELL EXPERIMENT
CC-2-2 [A, NaCl (0.01N.)/A/NaCl (0.1N.), A]

I ELECTRODES UNSHORTED, 0.1N. NaCl IN BOTH
II 0.01N. NaCl IN ONE ELECTRODE, 0.1N. IN OTHER
III 0.1N. NaCl IN BOTH ELECTRODES
IV ELECTRODES SHORTED TOGETHER, 0.1N. NaCl IN BOTH

was introduced into the cell, the potential would rise sharply, level off, and then gradually decrease. After a short time (5 to 15 minutes) valve V3 would be closed and valve V2 opened to put 0.1 N solution on both sides of the membrane again. The potential would then drop to some value close to zero, giving a small bias potential, and drift slowly toward zero. The concentration potential was taken as the sum of the potential at the end of step 2 and the bias, as shown in Figure 12. After the concentration potential had been determined for one electrode pair, the electrodes were shorted to remove any bias. The measuring procedure described above, except for conditioning, was repeated.

Preparation of Electrodes

All the electrodes were prepared from aqueous dispersions of carbon. The carbon was deposited on the Dacron felt backing material and fixed in the manner described in Part I.

Three carbons were used. They were Aquadag, which has been described previously; Dixon's Air Spun Graphite, Type 200-10; and Norite-A obtained from W. H. Curtin Company.

Aquadag came from the manufacturer in a predispersed form. All other carbons were dispersed in the laboratory with various agents. A method of dispersing carbon with tannic acid (TA) is described by Blair.[9] Other dispersants were used in a similar manner.

Another dispersing agent used was the sodium salt of

polystyrenesulfonic acid (PSA) obtained as Lustrex S-710 from Monsanto Chemical Company. This material yielded good dispersions at a low concentration of dispersant. However, the carbon material was easily washed off of the finished electrode by water. Various techniques were tried to fix the graphite on the patch. A concentrated sodium chloride dip was partly effective, as was concentrated HCl, followed by thorough rinsing and drying. Although electrodes obtained by this method were sufficiently stable for concentration cell experiments, it was felt that further investigation of this material was not justified.

Poly-N-vinylimidazole methiodide (PVI-I) was prepared by quaternizing poly-N-vinylimidazole (PVI) (Badische Anilin und Soda Fabrik AG, Ludwigshafen, Germany) with methyl iodide. The quaternizing method was that given by Blair[9] which was a modification of the method of Gregor and Gold.[30] The iodide salt was found to be an effective graphite dispersant; before quaternization no dispersing property was evident.

Poly-N-vinylimidazole was also quaternized with dimethyl sulfate after the procedure of Surrey.[31] The quaternization was carried out by adding 25 grams of PVI to 300 ml. of dimethyl sulfate (Eastman practical grade) in a 600 ml. round bottom flask. The flask was fitted with a calcium chloride drying tube and heated in an oil bath to 150°C for about 30 minutes. The product, which will be

referred to as PVI:SO_4, was filtered in a sintered glass Buchner funnel and washed with one liter of anhydrous ether in several portions. The hygroscopic product was stored in a vacuum desiccator without further purification. This material seemed to have the same dispersing properties as the PVI-I.

Two methods of pretreating carbons chemically before dispersion were used. In one case the carbon was heated in a mixture consisting of three parts sulfuric acid to one part nitric acid by volume. The other consisted of heating the carbon sample in fuming sulfuric acid (Oleum). The first method will be referred to as mixed acid treatment (MA) and the second as oleum treatment (O). The procedure used in these treatments is described by Blair.[9]

Results

The concentration potentials obtained with CC-2 are given in Tables 3 and 4. None of these potentials agrees with those predicted in Table 2 for electrodes responsive to only one ion type.

This can be explained by assuming the electrodes are partially responsive to both types of ions; that is, they are cation-anion responsive electrodes. The theory of cation-anion responsive electrodes will be discussed in the next chapter.

These electrodes can be classified as predominantly cation-responsive, predominantly anion-responsive, or

TABLE 3

CONCENTRATION CELL POTENTIALS

Experiment Number	Type of Membrane	Electrode Code	Potential (mv.)		
			Unconditioned	Oxidized	Reduced
CC-2-1	Anion	A	--	-102.5	-107.5
CC-2-4	Anion	A(OT)-TA	--	-105.0	--
CC-2-8	Anion	D(OT)-TA	- 97.5	-107.0	-105.0
CC-2-7	Anion	A-PSA	-107.0	-107.0	-108.0
CC-2-11	Anion	D-PSA	- 96.0	--	--
CC-2-14	Anion	D-PVI:I	- 14.5	- 20.0	- 20.0
CC-2-15	Cation	D-PVI:I	--	+ 86.0	+ 90.0
CC-2-18	Cation	D-PVI:SO_4	--	+ 96.0	+ 97.0
CC-2-19	Anion	D-PVI:SO_4	--	- 11.5	- 10.0
CC-2-21	Cation	N-PVI:SO_4	+102.0	+103.0	+104.5
CC-2-22	Anion	N-PVI:SO_4	--	- 3.0	- 7.0
CC-2-20	Cation	A(MA)-PVI:SO_4	--	+ 29.0	+ 30.0
CC-2-23	Cation	A(MA)-PVI:SO_4	--	+ 52.5	+ 75.5

TABLE 4

CONCENTRATION CELL POTENTIALS

Experiment Number	Type of Membrane	Electrode Code	Potential (mv.)		
			Unconditioned	Oxidized	Reduced
CC-2-3	Cation	A-NC	--	+ 46.0	+ 58.0
CC-2-9	Cation	A-QS	+ 37.0	+ 35.0	--
CC-2-12	Cation	D-PSA-TMB	--	+ 32.0	--
CC-2-13	Cation	D-PSA-TMPD	+ 27.0	--	--
CC-2-16	Cation	D-PVI:I-TMPD	+103.0	+102.0	+102.5
CC-2-17	Cation	D-PVI:I-TMB	+101.0	+ 99.5	+101.0
CC-2-24	Cation	N-PVI:SO_4-DMPD	--	+106.5	+ 96.5
CC-2-25	Anion	N-PVI:SO_4-DMPD	--	- 5.0	- 4.5

intermediate-responsive according to how near the concentration potentials are to these predicted for perfect electrodes. Thus an electrode which developes potentials within ten or fifteen millivolts of -109.3 with an anion membrane or close to +1.6 millivolts with a cation membrane could be considered to be predominantly cation-responsive. Electrodes whose concentration potentials differ considerably from those predicted are classed as intermediate-responsive since they show considerable responsiveness to both types of ions.

Although the work done with CC-1 had indicated that electrical conditioning was necessary to activate the electrodes so that stable potentials could be obtained, the results of experiments with CC-2 showed that this is not necessary. The data shows that concentration potentials could be obtained in most cases from electrodes which were not conditioned. In general, however, the potentials were much more stable after conditioning than before.

Conditioning was retained as a standard procedure because it did yield more stable potentials. The results of demineralization studies[9] showed that the capacity of electrodes increased slightly with repeated cycling. This indicates that a certain amount of activation does occur. The conditioning procedure also assures that the electrodes are equilibrated with the solutions and should help to remove impurities.

Experiment CC-2-1 was a repeat of CC-1A-38 to check

the new cell and modified procedure. The potentials obtained in this experiment agree with the value of -106 mv. from CC-1A-38.

Oleum treated Aquadag and oleum treated Dixon's Air-Spun Graphite electrodes dispersed with tannic acid had been tested in demineralization cells[9] and were classified as cation-responsive. The potentials obtained with these electrodes in experiments CC-2-4 and CC-2-8 indicated predominant cation-responsiveness. This helped to confirm the reliability of the method.

Electrodes containing polystyrene sulfonic acid were studied in experiments CC-2-7 and CC-2-11. The addition of this polyelectrolyte to Aquadag seemed to increase the tendency toward predominant cation-responsiveness, as shown by potentials closer to -109.3 in CC-2-7 compared to CC-2-1. This slight difference, however, could be caused by experimental error. The potential developed in CC-2-11 shows that Dixon's Air Spun dispersed with PSA is also predominantly cation-responsive.

While these data are not sufficient to show that PSA increases cation-responsivity it does establish that this material can be used to prepare cation-responsive electrodes. Because of the difficulty of obtaining stable electrodes from dispersions containing PSA, as discussed under electrode preparation, the matter was not pursued further.

The electrodes tested in CC-2-14 and CC-2-15 were

prepared from graphite dispersed with polyvinylimidazole methiodide. The potentials developed indicate predominant anion-responsive behavior. This was the first anion-responsive electrode prepared, although demineralization cell data[9] showed very low anion capacities. Graphite dispersed with PVI:SO_4 also yielded predominantly anion-responsive electrodes (CC-2-18 and CC-2-19), as does Norite dispersed with PVI:SO_4 (CC-2-21 and CC-2-22).

These experiments indicate that the dispersing agent can influence the ion-responsive behavior of electrodes. Graphite dispersed with PSA(CC-2-11) and with tannic acid[9] gave cation-responsive electrodes as did Norite dispersed with tannic acid.[9]

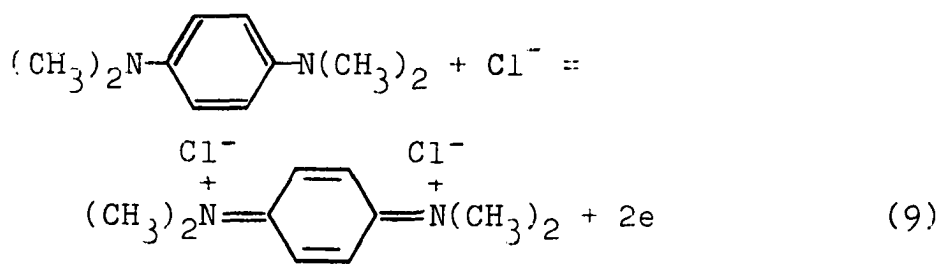
The type of carbon also has an effect as shown by CC-2-20 and CC-2-23. Mixed acid-treated Aquadag yields cation-responsive electrodes when dispersed with tannic acid.[9] Previous experience would indicate that dispersing this material with PVI:SO_4 should give predominantly anion-responsive electrodes. The potential developed in CC-2-20 shows intermediate-responsiveness with cation-responsiveness predominating. The electrodes were soaked in more PVI:SO_4 solution before experiment CC-2-23. The additional PVI:SO_4 enhanced the anion-responsiveness, but the electrodes were still intermediate.

Smith[27] has studied the effect of quaternized PVI dispersants. He found no evidence of a redox reaction

involving anions. He suggested that the dispersant may impart anion-responsive properties because it forms a permeable film containing fixed positive charges on the electrode surface; thus it may act as an anion-selective membrane.

Electrochemically Active Additives

Several organic compounds were added to carbon-based electrodes in attempts to increase anion-responsiveness. These molecules were capable of undergoing redox reactions involving anions. N,N,N',N' tetramethylphenylenediamine (TMPD) will be used as an example. Michaelis and coworkers[23] studied the oxidation of this compound in aqueous solutions. They found that the reaction proceeded stepwise with the formation of a semiquinone type compound as an intermediate. The net reaction is



(9)

Other compounds which might be expected to undergo redox reactions similar to (9) are: N,N,N',N' tetramethylbenzidine (TMB), N,N, dimethylphenylenediamine (DMPD), neocyanine (NC), and quaternized safranine.

These compounds did not yield the desired results when added to carbon electrodes. Electrodes prepared from

Dixon's Air-Spun Graphite dispersed with PVI:I yielded about the same potentials with TMPD (CC-2-16, Table 4) as without (CC-2-15, Table 3). The same is true of TMB (CC-2-17, Table 4). Norite dispersed with PVI:SO_4 yielded about the same potentials with DMPD added (CC-2-24 and CC-2-25, Table 4) as without (CC-2-21 and CC-2-22, Table 3).

Further evidence was obtained from demineralization cell experiments [27,37] which showed that electrodes prepared with quaternized PVI had the same anion capacities either with or without these compounds added.

The only evidence that indicated any effect of electrochemically active additives at all was obtained with electrodes that are cation responsive without additives. Dixon's Air-Spun Graphite dispersed with PSA yielded cation-responsive electrodes (CC-2-11, Table 3). The same materials with TMB and TMPD added gave electrodes of intermediate responsiveness (CC-2-12 and CC-2-13, Table 4). The same behavior was obtained with Aquadag electrodes with neocyanine and quaternized safranine added (CC-2-3 and CC-2-9, Table 4) compared to cation-responsive behavior obtained without the additives (CC-2-1, Table 3).

These compounds seem to add enough anion-responsiveness to convert a cation-responsive electrode to an intermediate responsive electrode. Their effect however, is insignificant when compared to that of quaternized PVI or other cationic polyelectrolytes.

Potentials Against a Reference Electrode

Potential drifts were present to some extent in all the experiments reported in this chapter. These drifts are difficult to interpret because they involve the potential difference between two carbon electrodes, both of which could be drifting. This difficulty can be overcome by observing the potential developed between a single carbon electrode and a reference electrode whose potential is stable.

Two cells were used for these studies. The first consisted of CC-2 and a glass H-cell. The two compartments of the H-cell were separated by a sintered glass disc. Carbon electrodes were placed in the four electrode positions of CC-2 as before, but the membrane was left out. One of the effluent tubes of CC-2 was plugged while the other was connected with Tygon tubing to a glass tube. The glass tube was inserted through a two-hole rubber stopper so that it almost reached the bottom of one side of the H-cell. The other hole of the stopper was fitted with tubing which conducted the effluent solution to a drain. Thus one compartment of the H-cell could be continuously flushed with the solution which flowed through the carbon electrodes and CC-2. The other half of the H-cell contained a saturated calomel electrode. The two compartments were connected by a saturated potassium chloride salt bridge. Both the salt bridge and the saturated calomel electrode were prepared from instructions given in an elementary laboratory text.[34] This cell will be called SCE-1.

The entire cell was immersed in a constant temperature water bath maintained at 25° C. The Sargent recorder and other auxiliary equipment used with CC-2 were retained for these experiments.

Demineralization cell DC-5, which is described elsewhere,[33] was also used. This cell contained one carbon and one silver-silver chloride electrode. The Sargent recorder was used for potential measurements and all other auxiliary equipment was that used in demineralization experiments.[33] Potential measuring experiments with this cell are designated Ag-1 to distinguish them from demineralization cell experiments.

Experiment SCE-1-1. Four Aquadag electrodes were placed in the concentration cell and conditioned at 0.85 v. in the usual manner. The conditioning process lasted for only one half-cycle of about thirty minutes and no current reversals were made. The conditioning was carried out with 0.02 N NaCl solution flowing through the cell. This flow was maintained slowly throughout the experiment. When the conditioning potential was removed the emf vs. the saturated calomel electrode of one of the oxidized and one of the reduced electrodes was measured. These electrodes will be referred to as 1(oxidized) and 3(reduced). Measurements were repeated on these two electrodes several times a day for six days. The time between readings was not recorded. Table 4 gives selected values of these measurements. The potentials

listed are those taken at the end of each day.

It will be noted that initially the oxidized electrode was positive with respect to the saturated calomel electrode and the reduced electrode was negative. The difference in potential between the oxidized and reduced electrodes is approximately equal to that imposed during conditioning. The potential of the oxidized electrode vs. the saturated calomel electrode became less positive with time while that of the reduced electrode became more positive. At the end of six days the potentials of the two electrodes differed by only 54 mv compared to 775 mv initially.

TABLE 5

EXPERIMENT SCE-1-1

	Oxidized mv	Reduced mv
Initial	+675	-100
1 day later	+326	+ 81
3 days later	+276	+160
4 days later	+270	+172
5 days later	+228	+174
6 days later	+218	+164

Note: Aquadag Electrode conditioned at 0.80 v in 0.02 N NaCl solution for 30 min. with no reversal. Cell: Hg,HgCl,/Sat KCl/0.02 N NaCl/Aquadag Electrode.

The potentials of the other electrodes, 2(oxidized) and 4(reduced), vs. the saturated calomel electrode were

measured occasionally throughout the course of the experiment. They behaved in a similar manner. At the end of the sixth day the potentials of these two electrodes vs. the reference electrode were +200 mv for the oxidized and +136 mv for the reduced.

Experiment SCE-1-2. At the end of SCE-1-1 all four electrodes were shorted together and left overnight, with 0.02 N NaCl in the cell. The electrodes were unshorted the next day and all four had potentials between +184 and +186 mv. The 0.02 N solution was replaced with 0.05 N solution and the potentials rose to between +201 and +203 mv.

These same four electrodes were then conditioned with 0.05 N NaCl solution flowing through the cell. The conditioning potential was 0.55 v. After thirty minutes, with no reversal of polarity, the conditioning current was less than one milliamp, indicating that the reactive sites on the electrodes were exhausted. The same electrode pair was oxidized in this conditioning procedure as in Experiment SCE-1-1.

After the conditioning potential was removed, the potential of electrode 1(oxidized) vs. the reference electrode was followed as a function of time. These data are given in Table 6 and plotted in Figure 10. The solution was left flowing throughout the experiment, with three interruptions as noted in Table 6.

The variation of potential with time in this experiment was very similar to that observed in Experiment SCE-1.

TABLE 6

EXPERIMENT SCE-1-2

Time in Hrs.	Potential of 1(oxidized) (mv)
0	710
2	540
4	480
6	446
8	410
10	390
12	378
14	370
16	364
18	360
20	354
22	348
25	334
*	-
31	324
32	316
34	312
36	306
38	302
*	-
50	296
52	284
54	282
56	280
*	-
62	-
65	276
82	256
101	234

*Solution flow stopped during these intervals. Reduced electrode - +118 after 101 hrs.

Note: A electrode conditioned at 0.55 v in 0.05 N NaCl. Cell: Hg, HgCl/Sat. KCl/0.05 N NaCl/Aquadag Electrode.

The potential decreased slowly. After 6 days it had returned to the same value obtained at the end of Experiment SCE-1-1 after 0.05 N solution was introduced and just before the electrodes were conditioned again.

After six days all four electrodes were shorted

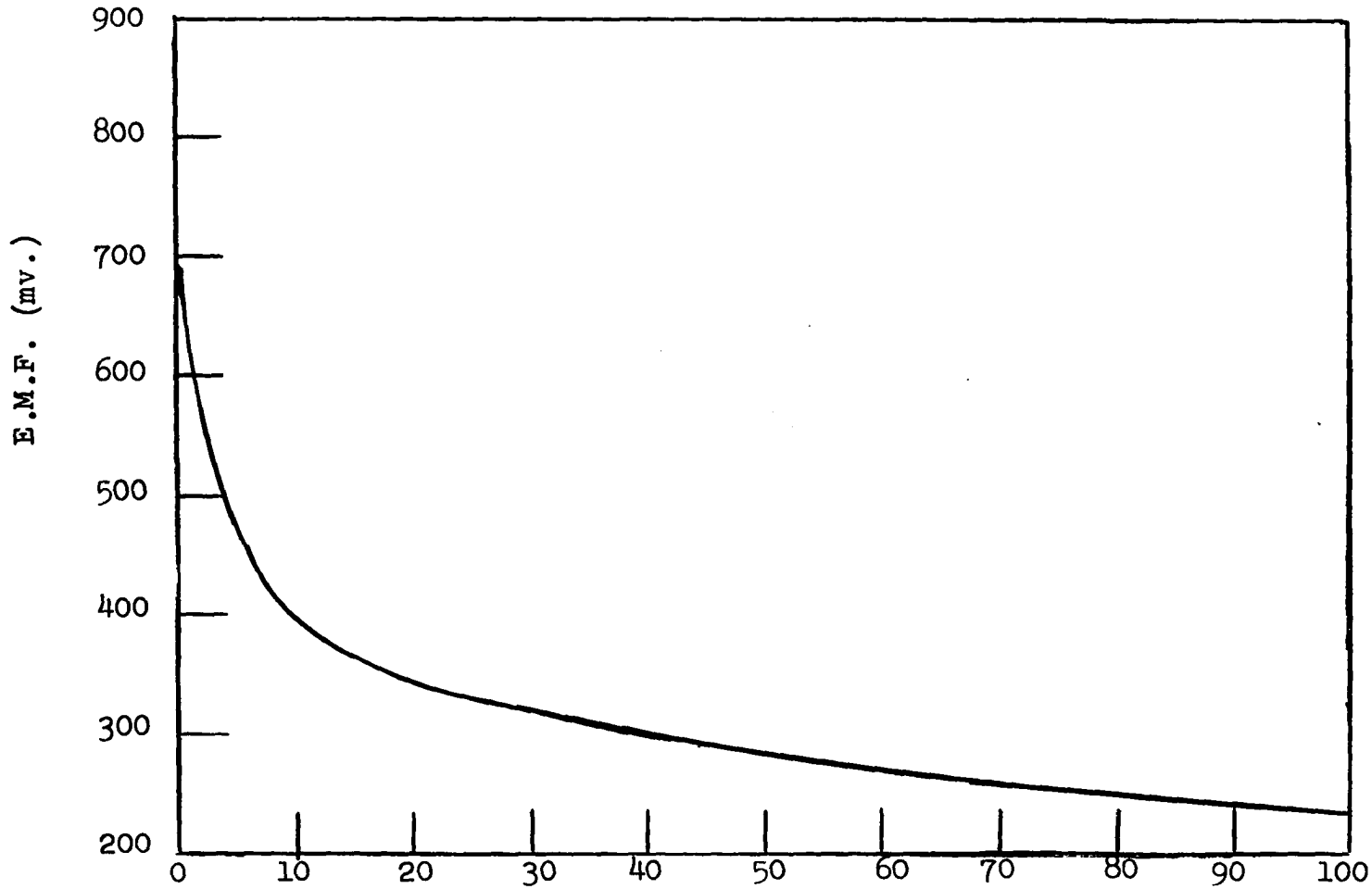


FIGURE 10

E.M.F. vs. TIME, EXPERIMENT SCE-1-2

AQUADAG ELECTRODE vs. REFERENCE ELECTRODE

together for several hours in 0.05 N solution. The potentials after shorting were:

1(oxidized) - +204 mv
2(oxidized) - +206 mv
3(reduced) - +206 mv
4(reduced) - +205 mv

Experiment CC-2-3. An anion-selective membrane was then placed in the cell. This placed electrodes 1(oxidized) and 3(reduced) in one chamber and 2(oxidized) and 4(reduced) in the other. A concentration-cell experiment was then carried out by flushing the 0.05 N solution from the chamber containing 2(oxidized) and 4(reduced) with 0.1 N solution, while the 0.05 N solution was left on the other side.

The concentration cell potential between 1(oxidized) and 2(reduced) was -29.5 mv. If the electrodes were perfectly cation-responsive, the expected potential would be -32.4 mv. The result indicates a predominantly cation-responsive electrode, as expected.

After CC-2-30 the compartment containing 2(oxidized) was flushed with 0.05 N solution. The potential of 1(oxidized) vs. the reference electrode was +205 mv compared to +204 mv before the experiment. The potential of 2(oxidized) vs. the reference electrode was +210 mv compared to +206 mv before the experiment. This indicated that changing the concentration of solution in contact with 2(oxidized) had caused a slight change of potential.

Experiment Ag-1-1. The Ag-1 series of experiments were performed by a coworker.[36] The carbon electrode was

made from a mixture of Norite and Dixon's Air Spun Graphite which had been mixed acid treated. The material was then dispersed with tannic acid. This type of electrode has been adopted as a standard cation electrode for more recent demineralization cell experiments and is referred to as a SK electrode. Details of its preparation are given elsewhere.[32,33]

Ag-1-1 was preceded by several demineralization cycles. Demineralization experiments[32,33] are equivalent to the conditioning cycles used in concentration cell experiments. One difference is that a silver-silver chloride electrode, instead of an identical carbon electrode, is used as a counter electrode. Also, the polarity is not reversed until after the effluent concentration is the same as the feed concentration. This usually requires several hours.

The experiment began after a demineralization cycle, with the carbon electrode in the reduced state. The potential applied during demineralization was 595 mv. and the concentration of the sodium chloride solution was 0.03 N

The cell was connected to the recorder. The applied potential was removed, and the cell potential was recorded for several days. The variation of potential with time is given in Table 7. At first the cell potential was the same as that applied during the last cycle with the carbon electrode negative. This corresponds to a negative cell potential by the sign convention given in Appendix II. This

TABLE 7

EXPERIMENT Ag-1-1
POTENTIAL DECAY OF A REDUCED CARBON
ELECTRODE VS AN Ag-AgCl ELECTRODE
AFTER DEMINERALIZATION AT 595 mv

Time (hrs)	E (mv)	Time (hrs)	E (mv)
0	-595	45	-24
5	-422	50	-15
10	-314	55	- 7
15	-219	60	- 2
20	-145	74	+11
25	- 96	79	+14
30	- 68	105	+37
35	- 48	115	+44
40	- 35	119	+46

potential decayed with time and leveled out at a positive value (carbon electrode positive) which agrees with the results of SCE-1-1 and SCE-1-2.

Experiments Ag-1-2 and Ag-1-3. These experiments were performed with a freshly prepared S.K. electrode. The electrode underwent several demineralization and regeneration cycles before Ag-1-2 and between Ag-1-2 and Ag-1-3. The potential was observed after a regeneration cycle during experiment Ag-1-2. Experiment Ag-1-3 was after a demineralization cycle using the same electrode as in Ag-1-2. Several cycles separated the two experiments.

The decay of potential with time for these two experiments is given in Tables 8 and 9. Positive potentials indicate that the carbon electrode was positive with respect to the silver-silver chloride electrode.

TABLE 8

EXPERIMENT Ag-1-2
POTENTIAL DECAY OF AN OXIDIZED CARBON ELECTRODE VS AN Ag-AgCl ELECTRODE AFTER REGENERATION AT 553 mv

Time (hrs)	E (mv)	Time (hrs)	E (mv)
0	+553	85	+230
5	+397	95	+222
15	+345	105	+215
25	+313	115	+210
35	+292	125	+204
45	+274	135	+200
55	+260	155	+192
65	+248	175	+187
75	+238	185	+185

TABLE 9

EXPERIMENT Ag-1-3
POTENTIAL DECAY OF A REDUCED CARBON ELECTRODE VS AN Ag-AgCl ELECTRODE AFTER REGENERATION AT 562 mv

Time (hrs)	E (mv)	Time (hrs)	E (mv)
0	-536	60	- 19
5	-389	80	+ 29
10	-327	100	+ 66
20	-224	120	+ 91
30	-134	140	+105
40	- 80	150	+117
50	- 29		

CHAPTER IV

THEORY OF CARBON ELECTRODE POTENTIALS

The experimental results reported in the previous chapter show three features concerning the behavior of carbon electrode potentials that need interpretation:

1. Concentration cell potentials of carbon electrodes did not agree with those predicted for electrodes responsive to one ion type.

2. The potentials of carbon electrodes against a reference electrode decayed after conditioning, returning to the value obtained before conditioning.

3. Concentration cell potentials drifted, apparently as a result of changing the solution concentration on one side of the cell to develop the concentration potential.

The values of the concentration potentials indicate that all the carbon electrodes studied are partially responsive to both types of ions and therefore would be classified as cation-anion-responsive electrodes. This has been confirmed in recent demineralization experiments[37] in which measurable cation and anion capacities on the same electrodes have been found.

Concentration Cell Potentials

Concentration cells have been employed for a number of purposes in the past[1-6] and offer a useful method of characterizing electrodes, including those which are cation-anion responsive. They are usually differentiated into cells with or without transference. As an example, the cell

$$A/NaCl\ (a_1)/C\text{-}C/NaCl\ (a_2)/A \quad (a_1 > a_2) \qquad (11)$$

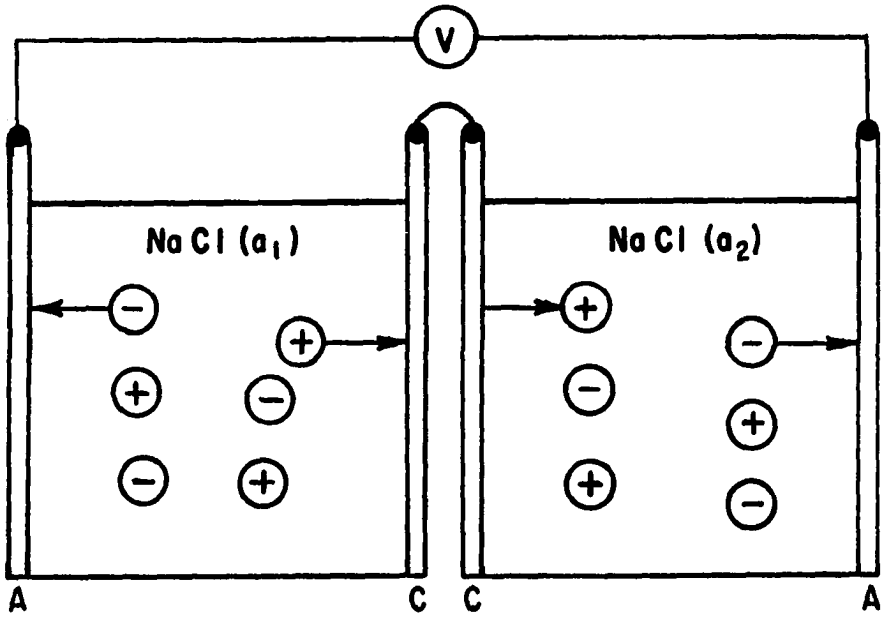
where A represents anion and C, cation-responsive electrodes would be a concentration cell without transference, while the cell

$$A/NaCl(a_1)/C_m/NaCl(a_2)/A \quad (a_1 > a_2) \qquad (12)$$

where C_m represents a cation - selective membrane would be a cell with transference. These two cells are illustrated schematically in Figure 11 with arrows indicating the direction of ionic migration (a result of electrode and membrane processes) under conditions of spontaneous discharge. The passage of one faraday of charge through cell (11) would transfer one mole of sodium chloride from compartment I to compartment II. The potential developed by this cell, operating reversibly, is

$$E = \Delta G/F = +(2RT/F)\ \ln\ (a_1/a_2) \qquad (13)$$

where ΔG represents the free energy of dilution of one mole



a – CONCENTRATION CELL WITHOUT TRANSFERENCE ($a_1 > a_2$)

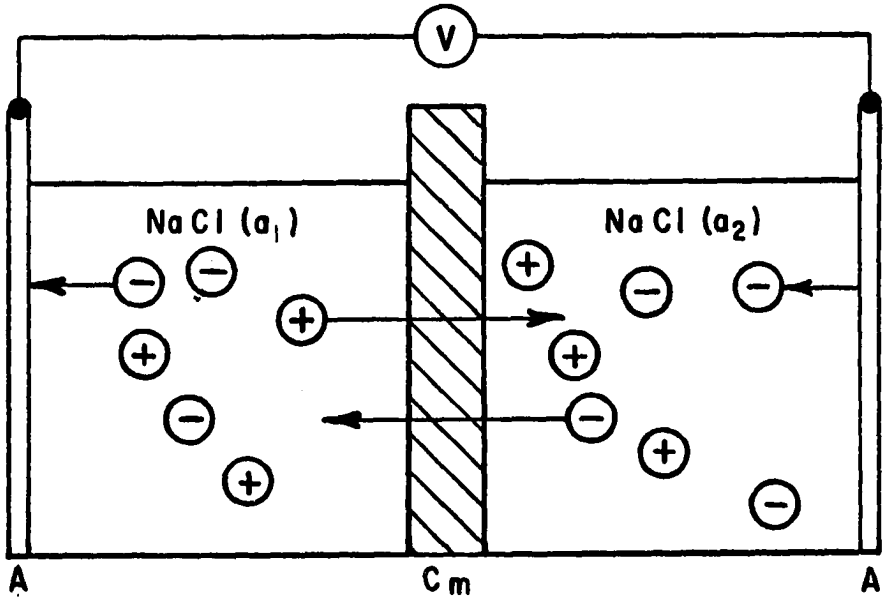


FIGURE II

b – CONCENTRATION CELL WITH TRANSFERENCE ($a_1 > a_2$)

A — ANION-RESPONSIVE ELECTRODES
C — CATION-RESPONSIVE ELECTRODES
C_m — CATION-EXCHANGE MEMBRANE
V — POTENTIOMETER

of sodium chloride.

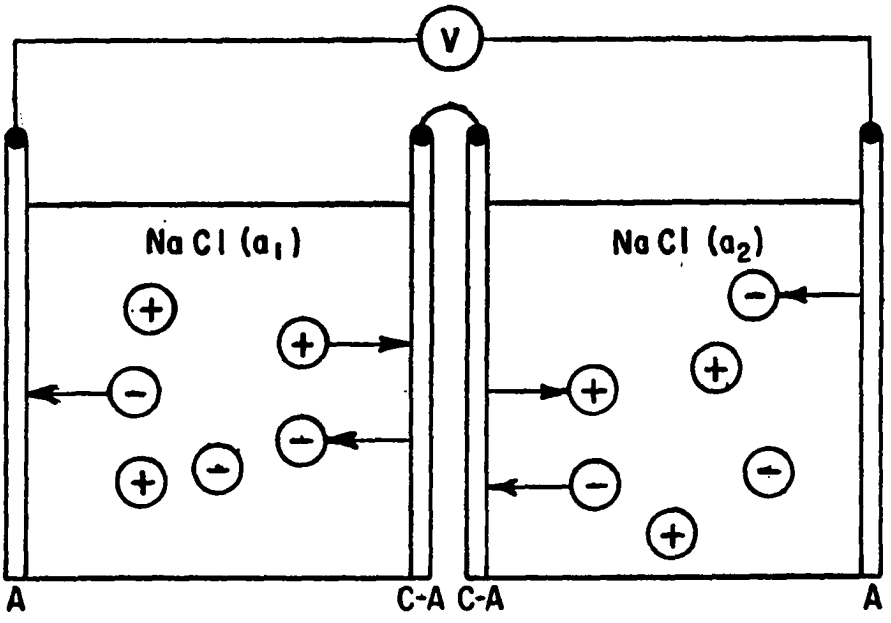
Reference to Figure 11 will show that one faraday of charge passed through cell (12) will transfer less than one mole of sodium chloride because of the migration of chloride ions through the membrane from compartment II to I. The number of equivalents transferred will be $(1 - t_-)$ where t_- represents the anion selectivity coefficient of the membrane. Since by definition $t_+ + t_- = 1$, the potential developed by this cell would be

$$E = t_+(\Delta G/F) = + t_+(2RT/F) \ln (a_1/a_2) \qquad (14)$$

The behavior of cation-anion responsive electrodes in concentration cells may be illustrated by considering the cell

$$A/NaCl(a_1)/C\text{-}A \quad C\text{-}A/NaCl(a_2)/A \quad (a_1 > a_2) \qquad (15)$$

where C-A represents cation-anion responsive electrodes. The directions of ionic migrations in this cell, given in Figure 12, show that this is also a cell with transference. The pair of cation-anion electrodes act as an interface separating the two compartments which allows passage of both types of ions from one compartment to the other. Therefore, the electrodes behave similarly to an ion-selective membrane; only in this case the ions are transported between compartments by electrode reactions and not ionic migrations. The fractions of the current carried by the transport of each ion can be



a - CONCENTRATION CELL WITH CATION - ANION ELECTRODES ($a_1 > a_2$)

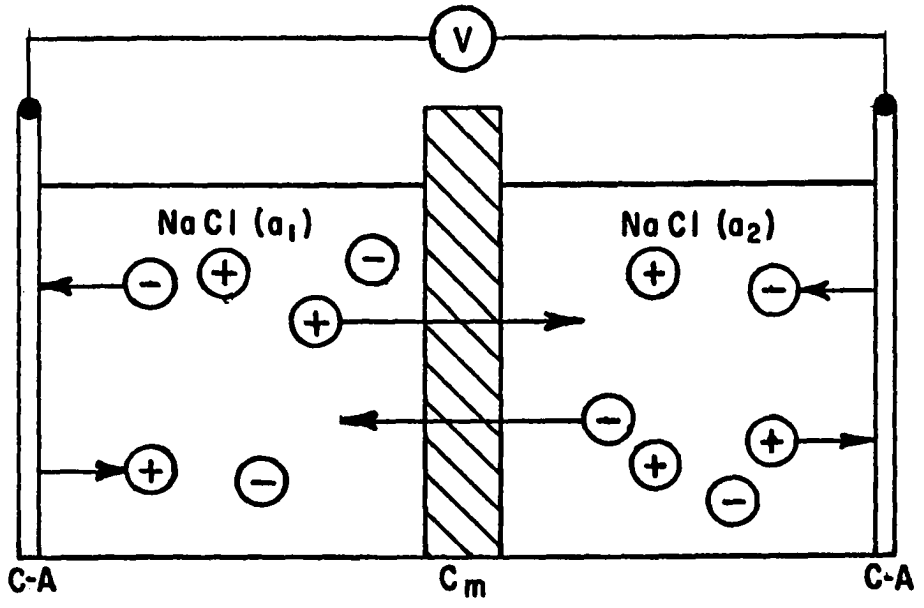


FIGURE 12

b - CONCENTRATION CELL WITH CATION - ANION ELECTRODE AND ION - EXCHANGE MEMBRANE ($a_1 > a_2$)

C-A — CATION-ANION RESPONSIVE ELECTRODE
A — ANION-RESPONSIVE ELECTRODE
C_m — CATION EXCHANGE MEMBRANE
V — POTENTIOMETER

expressed in terms of a selectivity coefficient similar to those used for membranes. The symbol τ will be used for electrode selectivity coefficients to distinguish them from t for membranes. The number of equivalents of sodium chloride transferred per faraday of charge, therefore, would be $1 - \tau_-$. The potential of this cell would be

$$E = -\tau_+(2RT/F) \ln (a_1/a_2) \qquad (16)$$

in analogy to equation (14). These selectivity coefficients may be regarded as transference numbers of ions across the solution electrode interface. They could in principle be determined by a Hittorf method.

The similarities between electrodes and membranes, which were developed in the above discussion, have long been recognized;[26,3] and membranes are sometimes described as ion-exchange electrodes.

The concentration cells used to characterize carbon electrodes in the present study contain both cation-anion-responsive electrodes and ion-selective membranes. The cell

$$C\text{-}A/NaCl(a_1)/C_m/NaCl(a_2)/C\text{-}A \quad (a_1 > a_2) \qquad (17)$$

is represented schematically in Figure 12(b). The arrows indicate ionic movement for the case where $\tau_+ > t_+$. The number of moles of salt transferred per faraday can be determined by considering the gain and loss of ions in compartment I. This compartment will gain t_+ and lose τ_+

equivalents of sodium ion as a result of the electrode and membrane processes. The change in chloride ion concentration will be the same to maintain electroneutrality, and the net transfer of salt will be $|(t_+ - \tau_+)|$. A similar consideration of cells composed of electrodes and membranes with all possible combinations of values of τ_+ and t_+ shows that the potential of any such cell is given by

$$(t_+ - \tau_+)(2RT/F) \ln (a_1/a_2) \qquad (18)$$

If cell configurations are always written so that a_1 is greater than a_2, the sign of the potential will be determined by the sign of the quantity $t_+ - \tau_+$.

Cation selectivity coefficients calculated for several carbon electrodes with equation (17) are given in Table 10. The membrane selectivity coefficients given in Table 1 and the concentration potentials from Table 3 were used in these calculations.

The selectivity coefficient of the electrode prepared from Dixon's Air-Spun Graphite dispersed with PVI:I was determined with both a cation- and an anion-selective membrane (Experiments CC-2-14 and -15). The results of the two experiments agree quite well. The same is true of the Air-Spun-PVI:SO_4 electrode (Experiments CC-2-18 and -19) and the Norite-PVI:SO_4 electrode (Experiments CC-2-21 and -22).

These results support the assumption that the difference between the measured potentials and those expected

for perfect electrodes (Table 2) are caused by cation-anion-responsiveness and not just experimental errors.

TABLE 10

SELECTIVITY COEFFICIENTS OF CARBON ELECTRODES

Experiment Number	Type of Membrane	Electrode Code	τ_+ Oxidized	Reduced
CC-2-1	Anion	A	0.94	0.98
CC-2-4	Anion	A(OT)-TA	0.96	--
CC-2-8	Anion	D(OT)-TA	0.98	0.96
CC-2-7	Anion	A-PSA	0.98	0.99
CC-2-14	Anion	D-PVI:I	0.19	0.19
CC-2-15	Cation	D-PVI:I	0.21	0.17
CC-2-18	Cation	D-PVI:SO_4	0.12	0.09
CC-2-19	Anion	D-PVI:SO_4	0.12	0.10
CC-2-21	Cation	N-PVI:SO_4	0.05	0.04
CC-2-22	Anion	N-PVI:SO_4	0.04	0.07
CC-2-20	Cation	A(MA)-PVI:SO_4	0.72	0.72
CC-2-23	Cation	A(MA)-PVI:SO_4	0.51	0.30

Potential Decay After Conditioning

Model of Carbon Electrodes

Carbon electrodes are unique because they exhibit the cation-anion selective properties of ion-selective membranes combined with many of the conductive and potential characteristics of ordinary electrodes. This suggests a simple model

which will be used to interpret the potential drifts encountered in this study.

A carbon electrode will be represented by two components; a perfect electrode which is reversible to only one type of ion and an imperfect membrane which has the same selectivity coefficient ($\mathcal{T}_+$) as the carbon electrode.

This model may have some relationship to the physical nature of the carbon electrodes studied. Smith[27] has suggested that the polyelectrolytes used as dispersants may form a film on the carbon surface and act as an ion-selective membrane. It is possible that the polyelectrolytes and the fixed charges of the surface oxygen groups on the carbon surface account for the membrane-like behavior of the electrodes. The model, however, does not have to be an accurate description of the physical character of the electrodes to be useful in treating the potential decay phenomena.

Equivalent-Circuit Model. An extension of the equivalent-circuit model of transference cells proposed by Murphy[35] will be applied to the model discussed above. A brief digression is required to introduce this concept.

The equivalent-circuit model can be illustrated with the transference cell

$$\mathrm{Ag,AgCl/NaCl}(a_1)\mathrm{/Ag,AgCl} \qquad (19)$$

which is shown in three different aspects in Figure 13. In (a) the system is in equilibrium with a uniform concentration

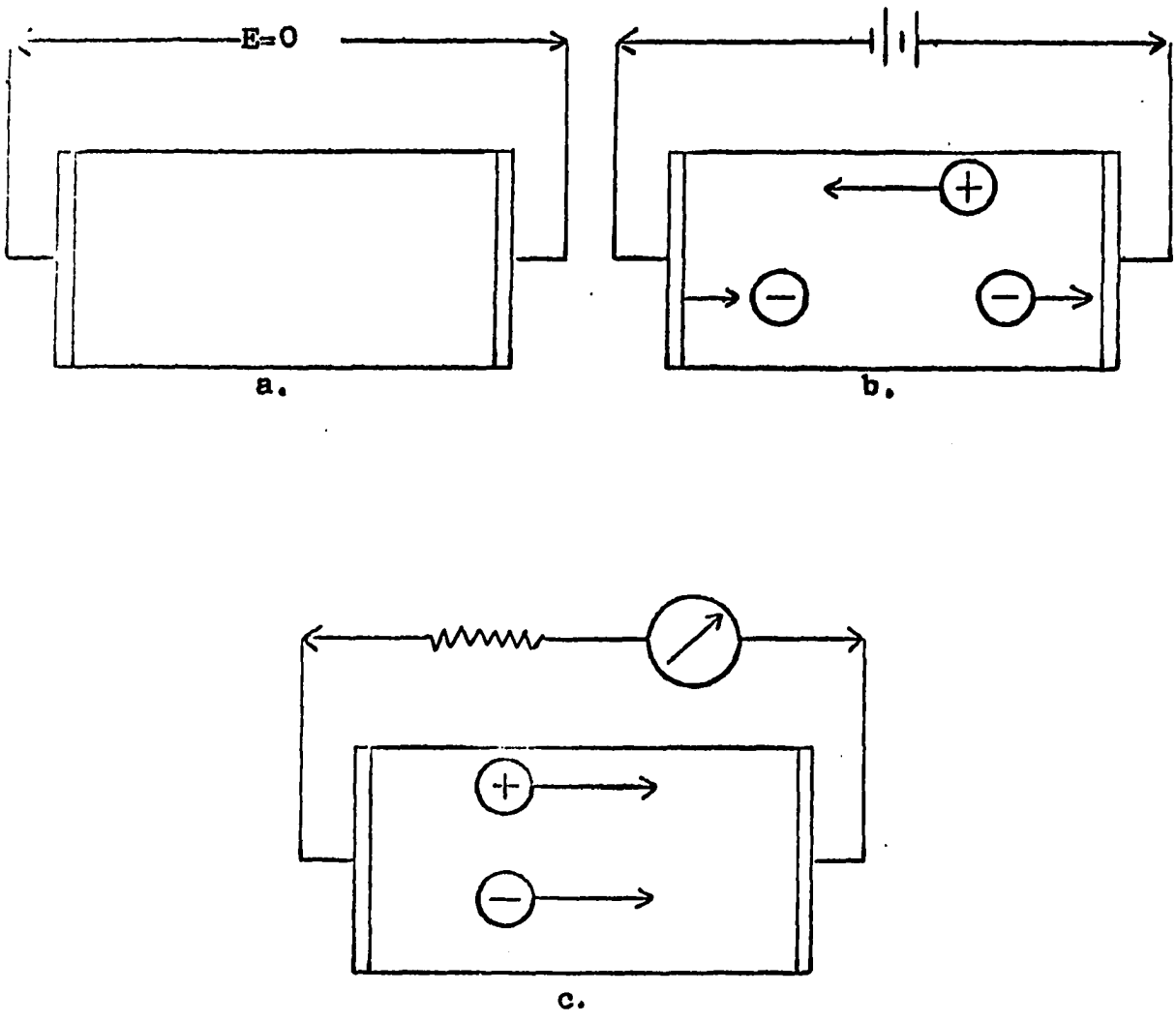


FIGURE 13

CROSS SECTIONS OF THE SIMPLE TRANSFERENCE CELL

double lines at end of cells represent silver - silver chloride electrodes.

(a) cell in equilibrium, concentration uniform; (b) cell with external applied voltage, representing "charging process; and (c) concentration cell with transference, emf being measured with high resistance voltmeter.

and no external voltage.

In (b) an external voltage has been applied causing current to pass through the cell. With the passage of current, chloride ions are consumed at the anode and produced at the cathode; and sodium ions migrate toward the cathode. This causes a concentration gradient across the cell with the lowest concentration at the anode and the highest at the cathode. In the ideal case, this concentration gradient would be linear when the steady state is obtained.

The cell is shown with the electrodes in vertical positions in Figure 13. In practice the concentration gradients would cause convection.[40] It will be assumed in the following discussion that convection currents are not present, which would be true if the cell were horizontal.

In 13(c) the external battery of (b) has been replaced with a high resistance voltmeter. If the voltmeter is a potentiometer, the current in the external circuit is vanishingly small.

The concentration gradient caused by a passage of current in (b) leads in (c) to the development of a concentration potential measured by the voltmeter. In other words, (c) is a concentration cell with transference.

The concentration gradient in (c) will decrease with time because of diffusion of electrolyte. This will cause a corresponding reduction in the concentration potential. Thus cell (19) can be "charged" by an external battery (b) and

"discharged" by internal diffusion (c).

The equivalent circuit of the transference cell is shown in Figure 14 (a). The qualitative considerations which led[35] to the model are as follows:

Cell	Equivalent Circuit
Current is carried by parallel movement of two charge carriers, Na^+ and Cl^- ions, with different ionic conductances, l_+ and l_-. The equivalent conductance Λ of the salt is $\Lambda = l_+ + l_-$.	There are two parallel arms in the circuit with different resistances, R_+ and R_-, where $R_+/R_- = l_-/l_+$.
The electrodes are "permeable" to Cl^- ions. (The electrode reaction consumes or liberates Cl^- ions).	Negative charge passes directly from the external source through R_-.
The electrodes are blocking to Na^+ ions. (The electrode reaction does not involve Na^+ ions).	Charges passing through R_+ are blocked from the external circuit by condensers (Fig. 13a).
A concentration gradient generates an external voltage.	A charged condenser leads to an external voltage.
A concentration gradient is self-equalizing by diffusion in the absence of an applied voltage.	In the absence of an applied voltage, a charged condenser will automatically discharge through R_+ and R_-.

It should be stressed that in this model all reversible phenomena of the cell are associated with the capacitors and all irreversible phenomena with the resistors.

In 14(b) the current corresponding to 13(b) is analyzed. The flow of negative charge (anions) through R_+ is electrically equivalent to a flow of positive charge (cations) in the opposite direction. The current in the external

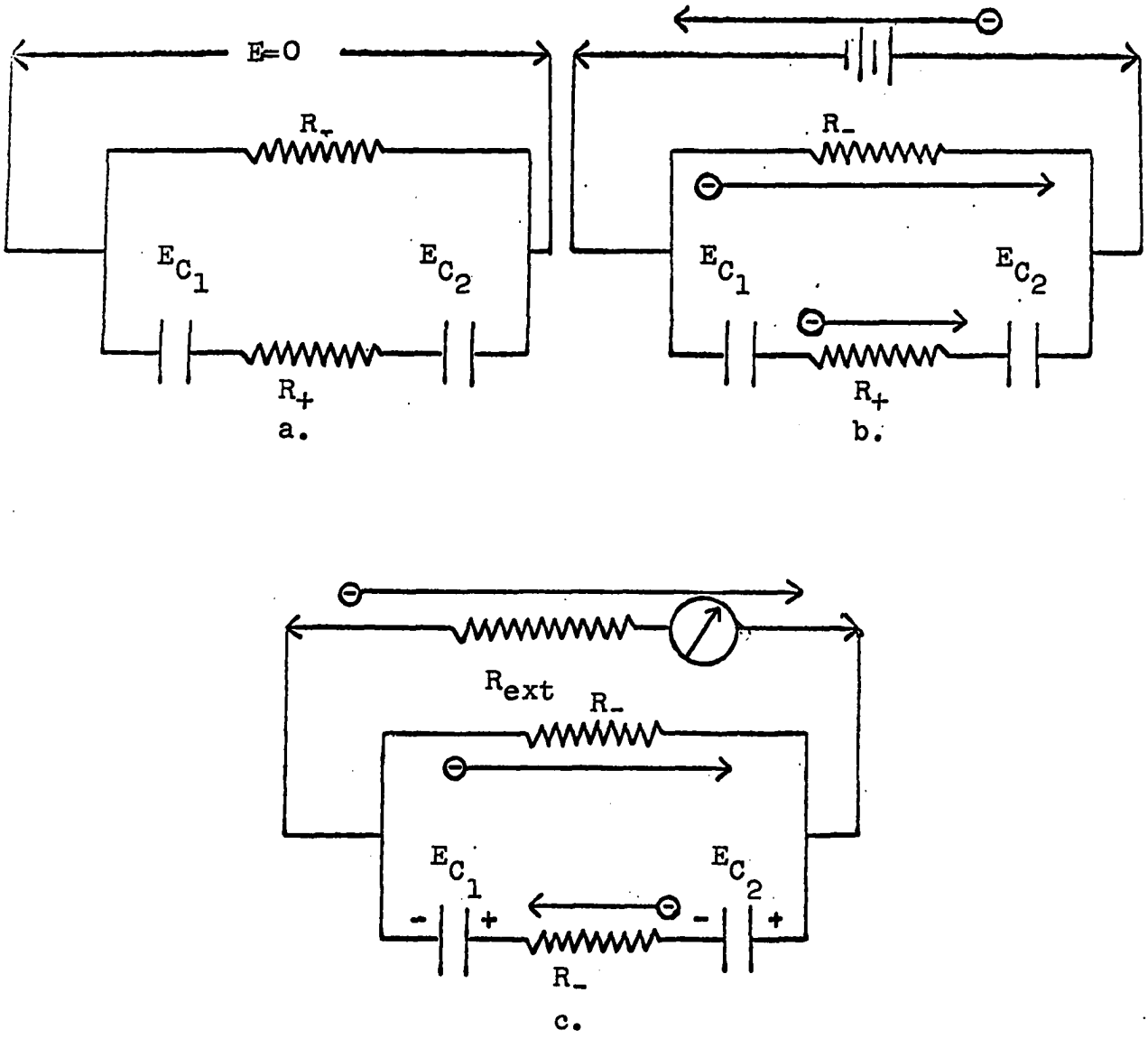


FIGURE 14

EQUIVALENT CIRCUIT CORRESPONDING TO CELLS OF FIGURE 13

(a) basic circuit; (b) charging with external source; and (c) internal discharge (free diffusion)

circuit is equal to the sum of the currents through R_+ and R_-.

The current during internal discharge of the cell is shown in Figure 14(c). The internal current is equivalent to free diffusion of salt, with the flux of positive ion equal to the flux of negative ion as required by the electroneutrality condition. From the electrical circuit standpoint, this means that the current through R_+ must be equal to that through R_-. Only an infinitesimal current flows through the external circuit to actuate the potentiometer.

The cell of Figure 14(a) could be discharged by short-circuiting the potentiometer. This is "external discharge," in contrast to the "internal discharge," of free diffusion which occurs whether an external circuit is present or not.

It has been shown[35] that if the circuit is equivalent to the cell:

$$E_c = E_{c_1} + E_{c_2} = 2(RT/F)\ln a_1/a_2 \qquad (20)$$

$$E_t = (l_+/l_+ + l_-)\, E_c = t_+E_c \qquad (20a)$$

Extension of the Equivalent-Circuit Model. In the original model, the potentials of the capacitors were assigned a zero value when the concentration of the solution was uniform throughout the cell. The capacitors were considered to be charged only when a concentration gradient existed.

While this is adequate for discussing cell (19), cells containing ion-exchange membranes require a more detailed relationship between charge and salt concentration.

The equivalent circuit for cell (19) can be modified by assigning a definite charge to each capacitor for each concentration of solution in contact with the electrodes. Then the charge on C_1 would be a function of the concentration of solution in contact with the left-hand electrode. The same relationship would hold for C_2 and the right-hand electrode.

The modified equivalent circuit is shown in Figure 15. The initial uniform concentration in the cell is illustrated in 15(a) by the capacitors having equal and opposite charges. Another condition is required to make the circuit equivalent to the cell. The initial potentials of the individual capacitors must be equal and opposite, or

$$E_c = E_{c_1} + E_{c_2} = 0 \qquad (21)$$

Therefore the effect of the charges is canceled and the circuit of Figure 15 is the same as the one shown in Figure 14. The only important difference is that the relationship between charge and concentration can be better understood with the second circuit.

In 15(b) the current corresponding to 13(b) is shown. The current from the external battery increases the charge on capacitor C_1 and decreases the charge on C_2. This

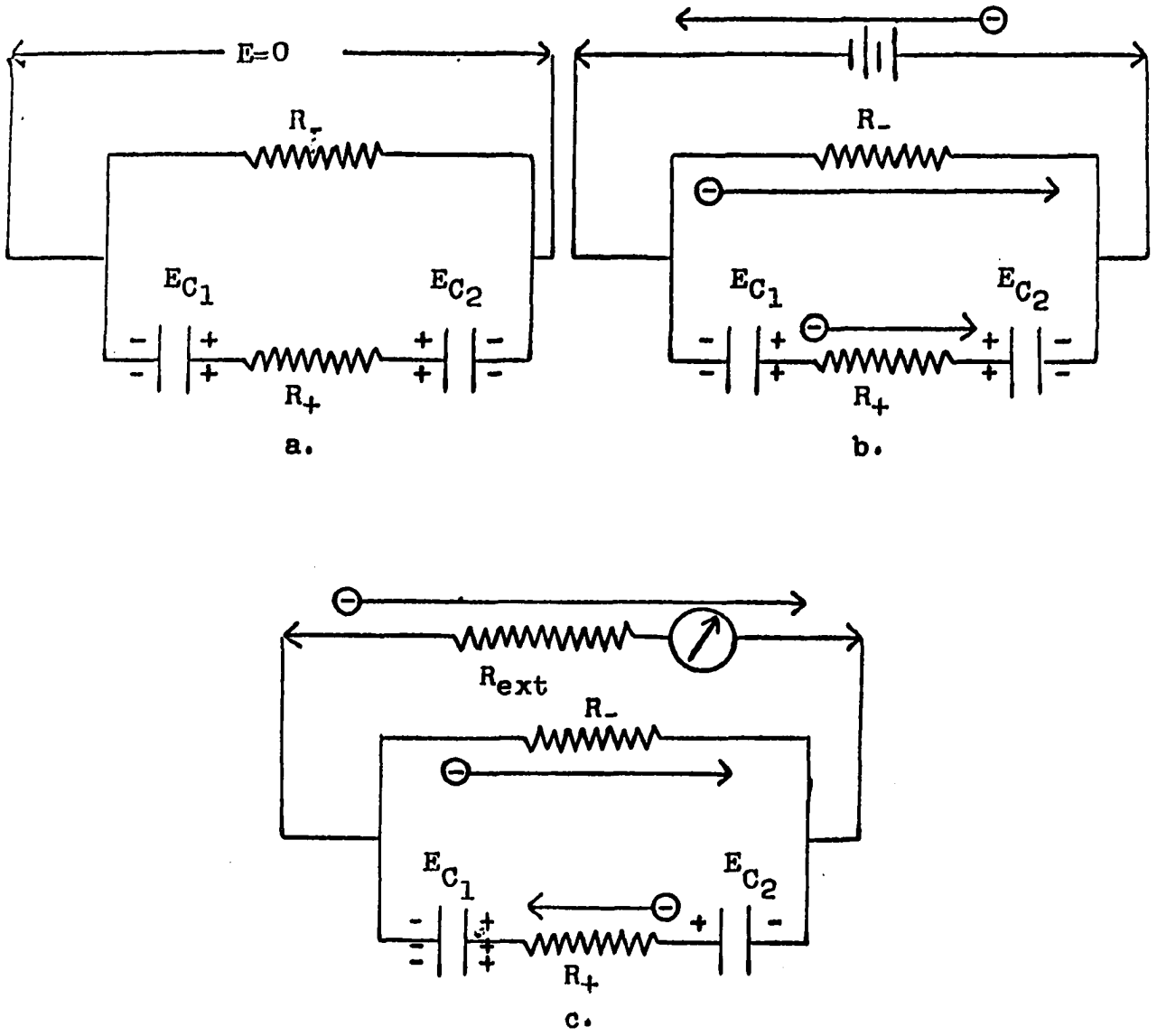


FIGURE 15

MODIFIED EQUIVALENT CIRCUIT RELATING CHARGE TO CONCENTRATION

original uniform concentration represented by equal and opposite charges on condensers; (a) cell in equilibrium; (b) charging with external source; and (c) internal discharge

corresponds to the increase of salt at the left-hand electrode and the decrease at the right.

The internal discharge by diffusion of 13(c) is represented in 15(c). The decrease in charge on C_1 and the increase on C_2 corresponds to the flow of salt from left to right in the cell. The current will flow until the circuit returns to the original state of 15(a). The potential relationships (20) and (20a) are obviously valid for both circuits.

An equivalent circuit such as shown in Figure 15 can also be used to represent the cell

$$Ag,AgCl/NaCl(a_o)/C_M/NaCl(a_o)/Ag,AgCl \qquad (22)$$

where C_M represents a cation-selective membrane. This is just cell (19) with a cation membrane between the two electrodes. There are many similarities between these two cells. A flow of current through cell (22) from an external battery would increase the concentration on the right, and decrease the concentration on the left-hand side. This concentration difference would decrease by diffusion after the battery is removed.

The resistances in the equivalent circuit of cell (22) would be a function of both the solution and membrane resistances. Thus,

$$R_+ = R_+^S + R_+^M \qquad (23)$$

$$R_- = R_-^S + R_-^M \tag{24}$$

where S and M represent the solution and membrane respectively.

The resistance to internal discharge is:

$$R_{int} = R_+ + R_- = R_+^S + R_-^S + R_+^M + R_-^M \tag{25}$$

Since the membrane has a high selectivity coefficient for cations:

$$R_-^M > R_-^S > R_+^M \tag{26}$$

$$R_-^M > R_+^S > R_+^M \tag{27}$$

Therefore R_-^M would be the largest term in equation (25) and would be the most important factor in determining the rate of internal discharge.

Since the resistance of the membrane is relatively constant with changing concentration, R_{int} should be fairly constant. This is not true for the simple transference cell without a membrane.

It should be emphasized that the resistance discussed above is the resistance of the cell to the internal discharge of free diffusion of electrolyte and not the resistance of the cell to current from the external circuit.

The resistance of the cell, as seen by the external circuit is obtained by a parallel combination of resistances

$$R_{cell} = R_+R_-/(R_+ + R_-) \qquad (28)$$

At low salt concentrations R_{cell} would be controlled by the solution resistance.

The salt concentrations of the solutions on either side of the membrane in cell (22) could be held constant by flowing solution of a given concentration through the cell. Thus, if solution with an activity a_o were flushed through the right-hand side of (22) during the "charging" and "discharging" process, only the concentration in the left-hand compartment would change. Because of the relationship between charge on the condensers and salt concentration discussed above, this is equivalent in the electrical circuit to connecting a battery across condenser C_2 as shown in Figure 16(a).

The "charging" and discharging steps are shown in 16(b) and (c). The potential of the battery is a function of the salt concentration on the right side and is

$$E_{C_2} = -\mathcal{E} = -2(RT/F) \ln a_o \qquad (29)$$

If the concentration of the left side changes to a value corresponding to an activity a_1 then,

$$E_{C_1} = 2(RT/F) \ln a_1 \qquad (30)$$

The measured (external) potential of the cell during internal discharge would be

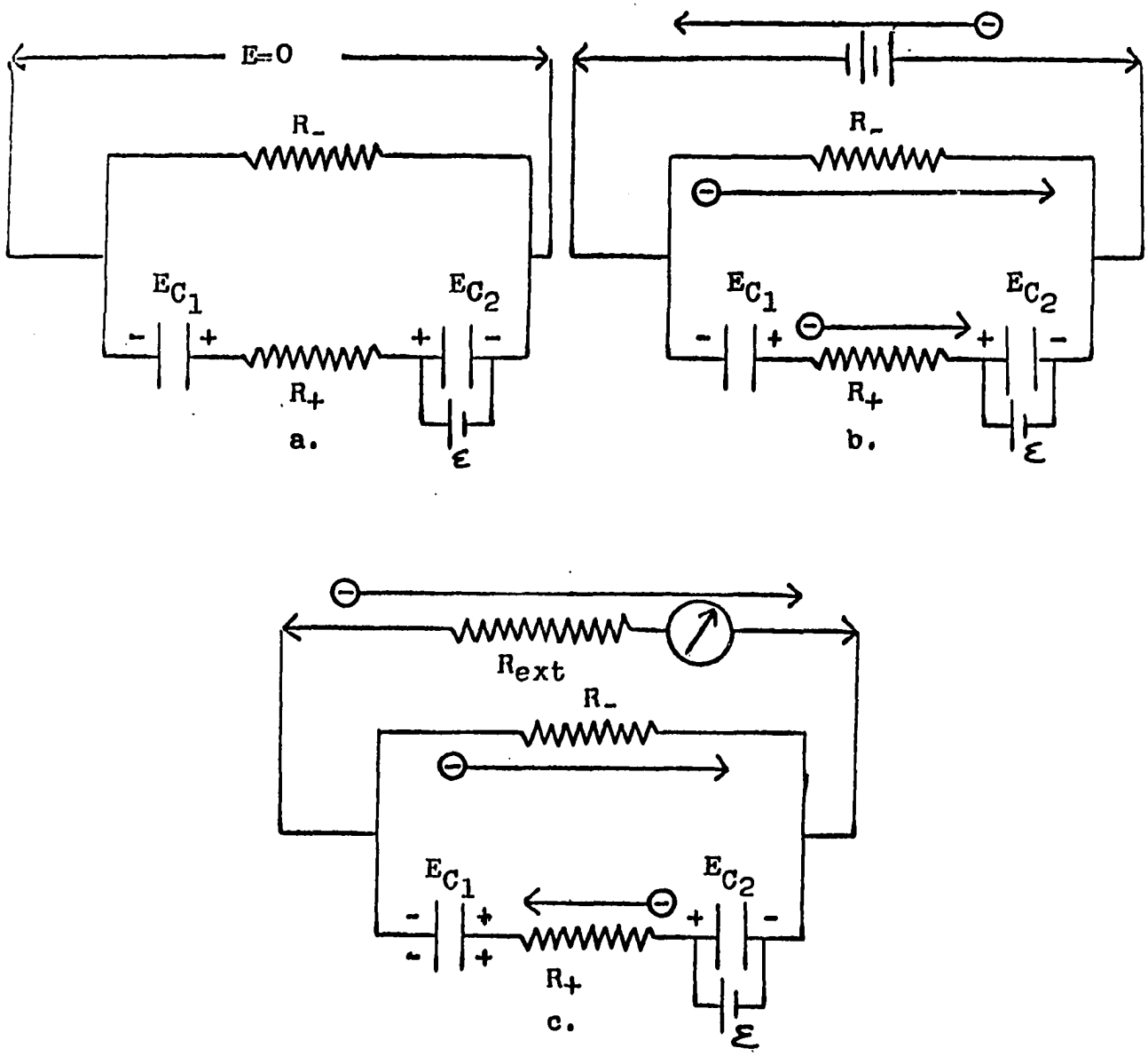


FIGURE 16

EQUIVALENT CIRCUIT OF CELL WITH ION-SELECTIVE MEMBRANE

constant concentration of right-hand compartment represented by battery in parallel with capacitor, (a) initial condition; (b) charging process; and (c) internal discharge

$$E_t = t_+(E_{C_1} + E_{C_2}) = 2t_+(RT/F) \ln (a_1/a_o) \qquad (31)$$

When the concentration in one compartment is held constant then the concentration change in the other compartment will be greater (for a given applied potential) than if the concentrations of both compartments were allowed to vary.

Another type of transference cell must be treated by the equivalent-circuit model before considering carbon electrodes. An example of this type of cell would be

$$Ag,AgCl/NaCl(a_o)/C_M/NaCl(a_o)/Hg_2Cl_2,Hg \qquad (32)$$

where the two electrodes are anion-reversible, but not identical. Usually the term transference cell is restricted to cells containing identical electrodes.[5] This seems an unnecessary restriction since cell (32) has all of the other properties of transference cells.

Passing current through (32) will produce a concentration gradient which will give rise to an open circuit potential. This potential is a function of the concentration difference and the transport properties of the ions across the membrane. The open circuit potential will decay because of internal diffusion.

There is an important difference, however. The open circuit potential of cell (32) does not decay to zero as would be the case if the electrodes were identical. Cell (32) is obtained by adding a cation membrane to the cell

$$Ag,AgCl/NaCl(a_o)/Hg_2Cl_2,Hg \qquad (33)$$

Cell (33) is not a transference cell and in the ideal case its potential is even independent of the salt concentration. The potential is a function of the Gibbs free energy change (ΔG) of the reaction:

$$Ag + (1/2)Hg_2Cl_2 = Hg + AgCl \qquad (34)$$

and

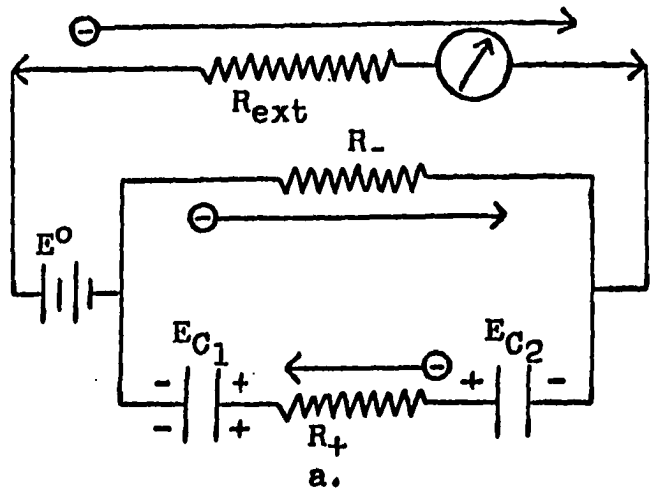
$$E = \Delta G/F = E^o \qquad (35)$$

The free energy of the cell reaction of (32) would be that of reaction (34) plus the free energy of dilution of t_+ moles of sodium chloride. If enough current were passed through (32) to change the concentration of salt in one compartment from a_o to a_1 and the other to a_2 the open circuit potential of the cell would be

$$E = E^o + t_+(2RT/F) \ln (a_1/a_2) \qquad (36)$$

where E^o is the potential of cell (33).

An equivalent circuit for cell (32) is shown in Figure 17. The case where the concentration in both compartments are allowed to vary during the "charging" process is illustrated in Figure 17(a). This circuit is just the circuit of Figure 15 with a battery added. The potential of the battery is E^o. After charging the cell the open circuit potential as measured by an external voltmeter would be given by



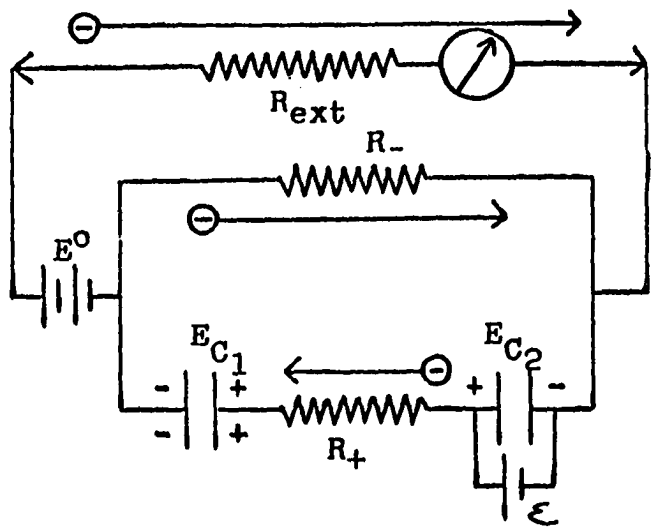


FIGURE 17

EQUIVALENT CIRCUIT OF TRANSFERENCE CELLS WITH DISSIMILAR ELECTRODES

(a) internal discharge, concentration of both compartments varying
(b) internal discharge, concentration of right-hand compartment constant

equation (36). After internal discharge is completed the potential would be E^{o}.

Figure 17(b) shows the equivalent circuit of cell (33) when the salt concentration in the right hand compartment is held constant. This is the same as the circuit of Figure 16 with the battery added because the electrodes are not identical.

Equivalent-circuit model for carbon electrodes. The model chosen to represent carbon electrode was discussed briefly before. It consists of a perfectly reversible electrode coupled with an imperfect membrane. For a cell containing a predominantly cation responsive electrode and a silver-silver chloride electrode (cell Ag-1).

$$\text{Cation Electrode/NaCl}(a_o)\text{/Ag, AgCl} \qquad (37)$$

the representation would be

$$\text{A/NaCl}(a_o)\text{/}C_M\text{/NaCl}(a_o)\text{/Ag,AgCl} \qquad (38)$$

Since the anion-reversible electrode (A) is not identical with the silver-silver chloride, this cell is similar to cell (32), and could be represented by the circuits of Figure 17.

Since fresh NaCl solution of constant composition was flushed through the cell during potential experiments using cell Ag-1, 17(b) would be the correct representation.

The conditioning process of repeated regeneration and

demineralization cycles would correspond to the charging of the condenser (concentration changes in the left-hand compartment).

The open circuit potential measurements correspond to the internal discharge phase of the equivalent circuit. This is the phase that must be explained to account for the potential decay.

Since the internal resistance is relatively constant (equation 25), the internal circuit can be treated as approximately linear.

For a linear circuit the potential of the capacitor E_{c_1} can be found by standard methods for electrical circuits.[38] Kirchoff's second law for the internal circuit is

$$\mathcal{E} - E_{c_1} - I_{(int)} R_{(int)} = 0 \qquad (39)$$

where $I_{(int)}$ is the internal current (corresponding to diffusion), and $R_{(int)}$ is given by equation (25).

Equation (39) may be integrated, using the proper boundary conditions,[38] to give

$$E_{c_1} = E^i_{c_1} e^{-t/RC} + (1-e^{-t/RC})\mathcal{E} \qquad (40)$$

where R is $R_{(int)}$, C is the capacitance of capacitor C_1, and $E^i_{c_1}$ is the potential of C_1 when t = 0 (after the charging process).

Equation (40) may be rewritten as

$$E_{c_1} = (E^i_{c_1} - \mathcal{E})e^{-t/RC} + \mathcal{E} \tag{41}$$

or

$$E_{c_1} = Be^{-t/RC} + \mathcal{E} \tag{42}$$

where $B = (E^i_{c_1} - \mathcal{E})$.

The measured potential of the self-discharging cell is just E_t, that of a concentration cell with transference. From Figure 17(b) it can be seen that

$$E_t = E^o + E_- = E_{c_1} - E_+ - \mathcal{E} + E^o \tag{43}$$

where E_+ and E_- represent the potential drop across the resistors. Since

$$E_+ = \tau_-/\tau_+ E_-$$

$$E_t = E_{c_1} - (\tau_-/\tau_+)E_- - \mathcal{E} + E^o \tag{44}$$

and

$$(E_t - E^o)(1 + \tau_-/\tau_+) = E_{c_1} - \mathcal{E} \tag{45}$$

$$E_t - E^o = \tau_+(E_{c_1} - \mathcal{E}) = \tau_+ Be^{-t/RC}$$

if τ_+ is constant we may write (46) as

$$E_t - E^o = Ae^{-t/RC} \tag{47}$$

or

$$\log(E_t - E^o) = -mt + \log A \qquad (48)$$

where $m = 1/(2.303)RC$ and $A = \tau_+(E^i_{c_1} - \mathcal{E})$

Test of Theory. If the theory is valid then equation 47 should be capable of fitting experimental potential decay data. This type of data is available in Tables 7, 8 and 9.

The method of Guggenheim (39) was used to evaluate 1/RC. If times t_1, t_2, t_3, etc., and $t_1 + \Delta$, $t_2 + \Delta$, and $t_3 + \Delta$, etc., are selected where Δ is a constant increment of time, it follows from equation (47) that

$$E_1 - E^o = Ae^{-t_1/RC} \qquad (49)$$

and

$$E_1' - E^o = Ae^{-(t_1+\Delta)/RC} \qquad (50)$$

where E_1 and E_1' are potentials at t_1 and $t_1 + \Delta$ respectively. Similar equations can be written for E_2 and E_2'. Subtracting (50) from (49) gives

$$E_1 - E_1' = Ae^{-kt_1(1-e^{-k\Delta})} \qquad (51)$$

where $k = 1/RC$. Equation (51) can be rearranged to give

$$kt_1 + \ln(E_1 - E_1') = \text{a constant} \qquad (52)$$

which can be generalized by dropping the subscript 1.

Figure 18 shows a plot of log $(E_t - E_{t+\Delta})$ vs t for the data given in Table 8. A Δ value of 30 hours was used. The points for the last part of the experiment fall on a straight line as predicted by equation (52). The points for the first 30 or 40 hours, however, deviate considerably from linearity. This was observed in the data from all three experiments and will be discussed later.

The best fit straight line was drawn through the points past 30 hours and 1/RC was calculated from the slope by the relation

$$\text{slope} = -1/(2.303)RC \tag{53}$$

With the value of 1/RC known E^o can be calculated from equation (47), since

$$(E_1 - E^o)/(E_2 - E^o) = e^{-(t_1-t_2)/RC} \tag{54}$$

E^o was evaluated with several sets of points within the linear region of the log $(E_t - E_{t+\Delta})$ plot and an average value obtained.

The constant A was then evaluated by plotting log $(E_t - E^o)$ vs t and extrapolating to zero time. This is illustrated in Figure 19 for Experiment Ag-1-2.

The values of the constants calculated from equation (47) for the three potential drift experiments are given in Table 11. The theoretical curves calculated for these

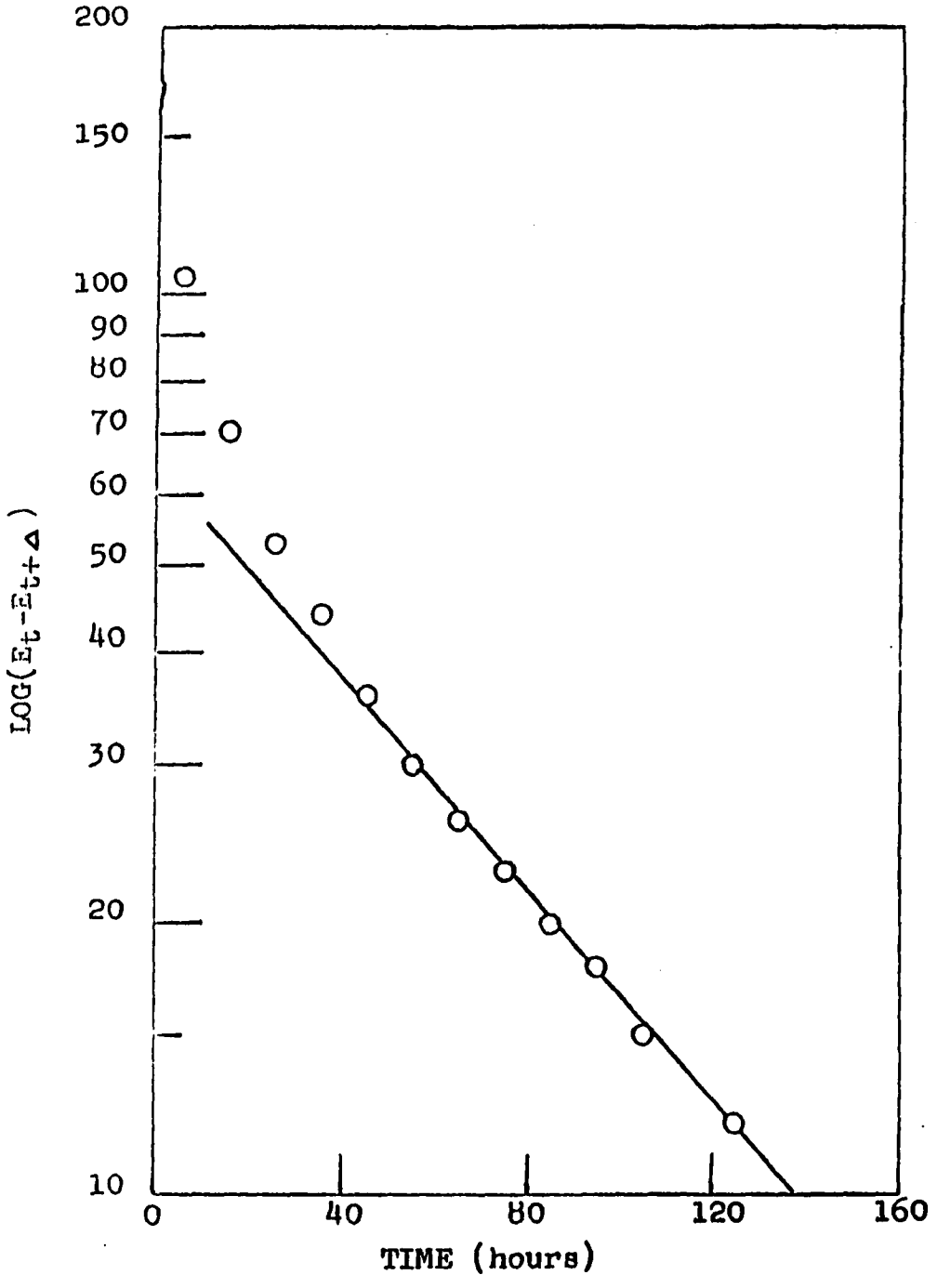


FIGURE 18

$LOG(E_t - E_{t+\Delta})$ vs TIME FOR Ag-1-2

= 30 hours, 1/RC = (2.303) slope = 0.015 hours^{-1}

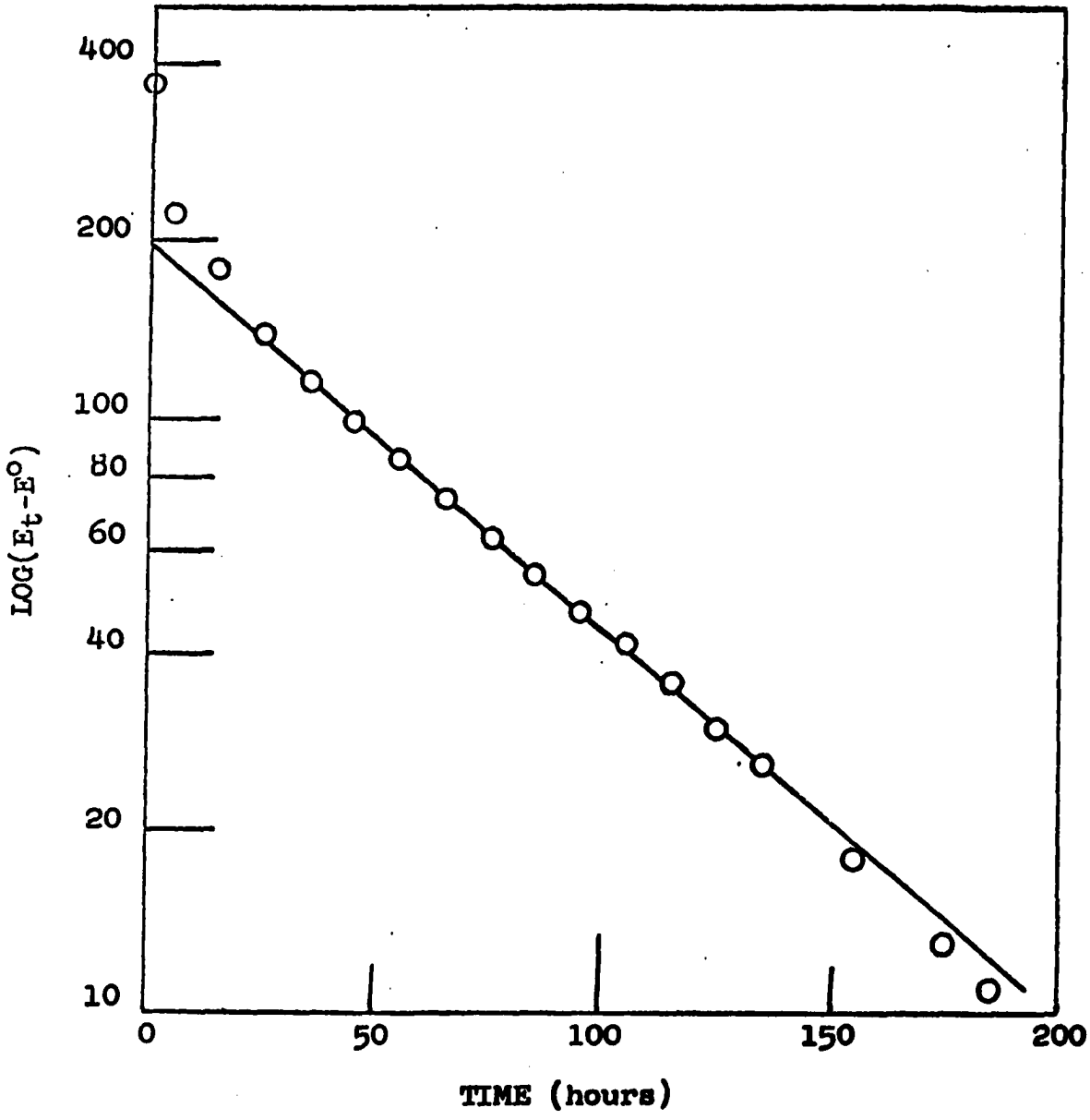


FIGURE 19

LOG(E_t-E^o) vs TIME FOR Ag-1-2

E^o = +174 millivolts, A = +198 millivolts,
1/RC =(2.303) slope = 0.015 $hours^{-1}$

experiments are shown in Figures 20, 21 and 22. The points are experimental, from Tables 7, 8 and 9. The agreement is quite good in all three cases, except for the first few hours of each experiment.

TABLE 11

CONSTANTS CALCULATED WITH EQUATION (47)

Experiment No.	$1/RC(hr^{-1})$	E^{o}(mv)	A(mv)	$E_{app}-E^{o}$(mv)
Ag-1-1	+0.023	+ 55	-224	-650
Ag-1-2	+0.015	+174	+198	+379
Ag-1-3	+0.015	+174	-470	-710

Experiments Ag-1-2 and Ag-1-3 were successive experiments on the same electrode. The calculated values of $1/RC$ and E^{o} were the same for both experiments as would be expected.

Standard cation (S.K.) electrodes were used for all three experiments; however, the one used in Ag-1-1 was considerably older, had gone through more than 100 cycles and had been stored for several months before being used in this experiment. The electrode used in Ag-1-2 and Ag-1-3 was freshly prepared and had been through less than ten cycles before the experiments. This may account for the difference between the constants calculated for the different electrodes. It is also possible that no two electrodes can be prepared that are exactly identical. This is born out by

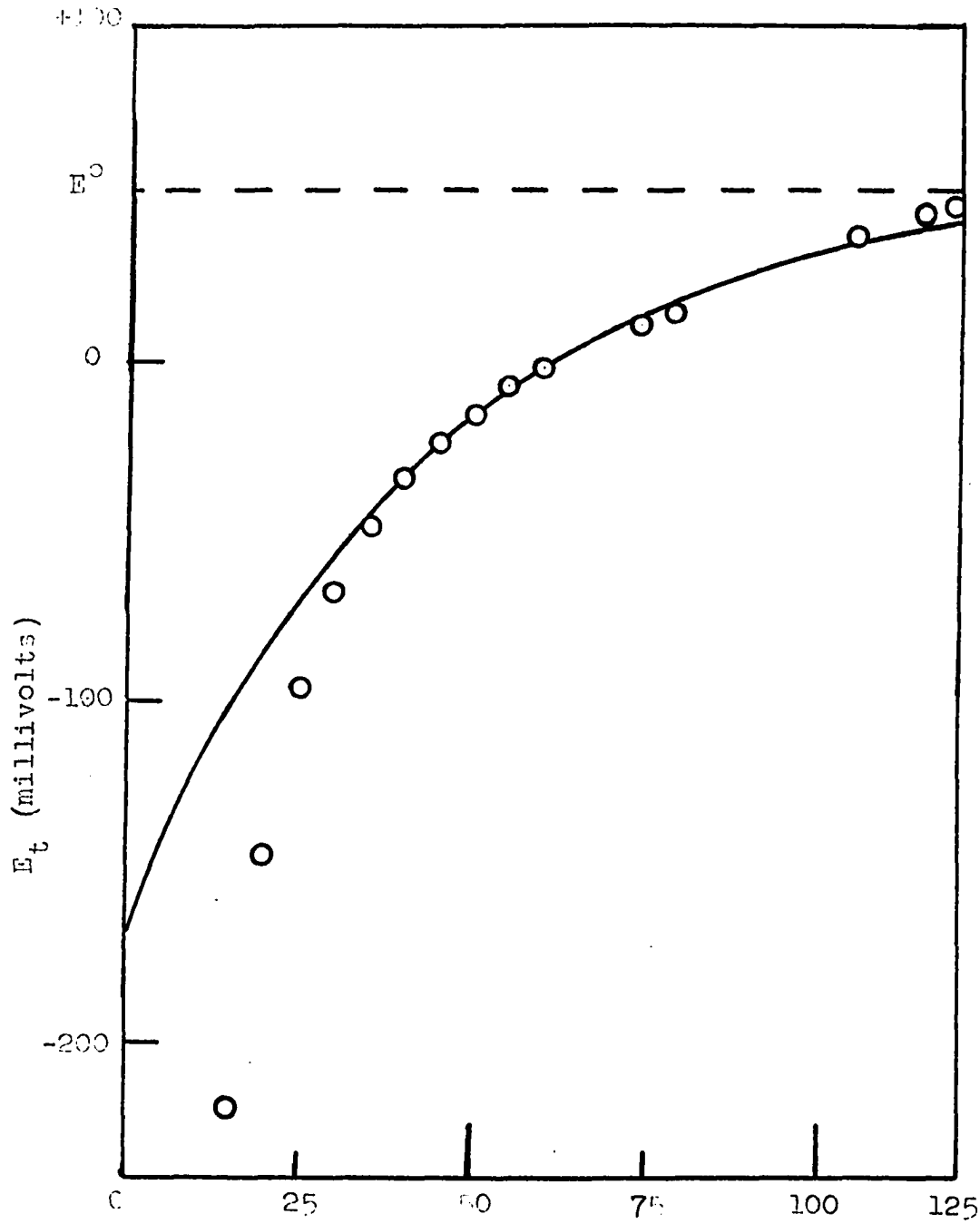


FIGURE 20

E_t vs TIME FOR Ag-1-1

The line is calculated from equation 49, A = -224 millivolts E° = +5 millivolts, 1/RC = 0.023 hours^{-1}; the points are experimental.

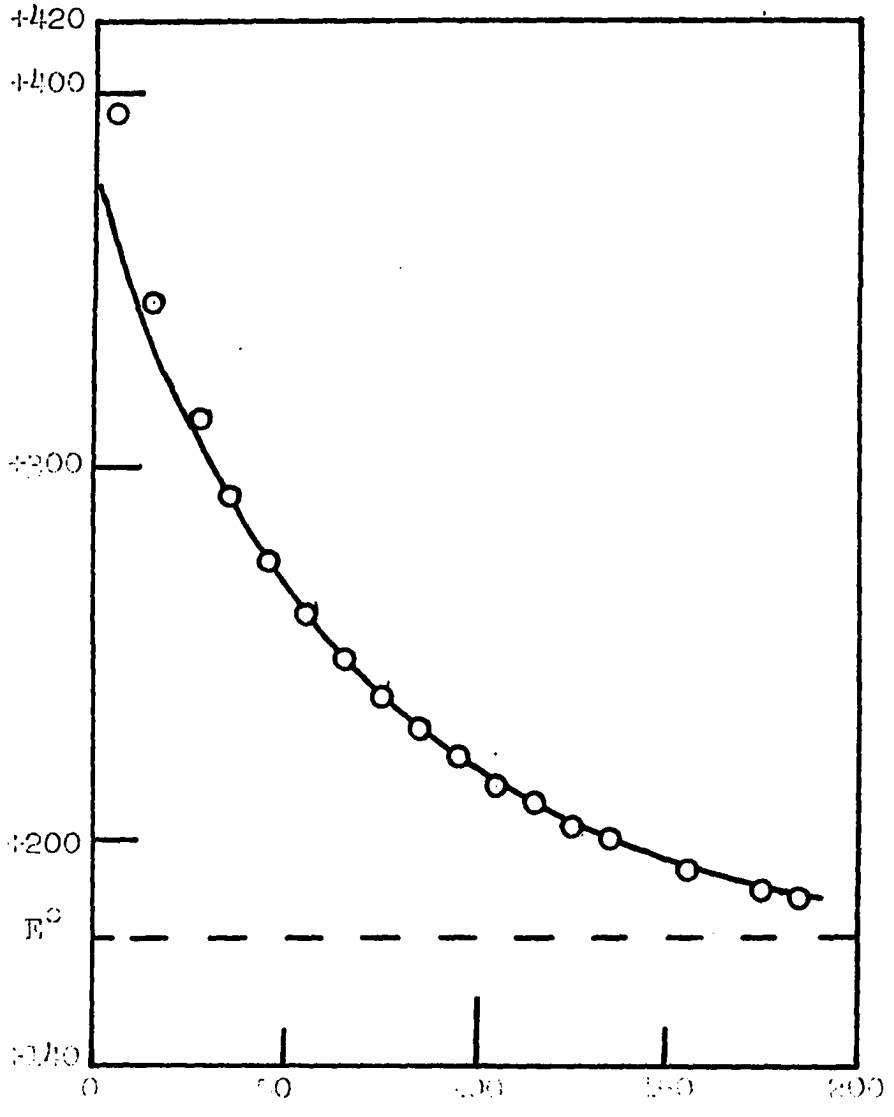


FIGURE 21

E_g vs TIME FOR Ag-1-2

The line is calculated from equation 20, β = +198 millivolts E° = +202 millivolts. 1/RC = 0.015 hours^{-1}; the points are experimental.

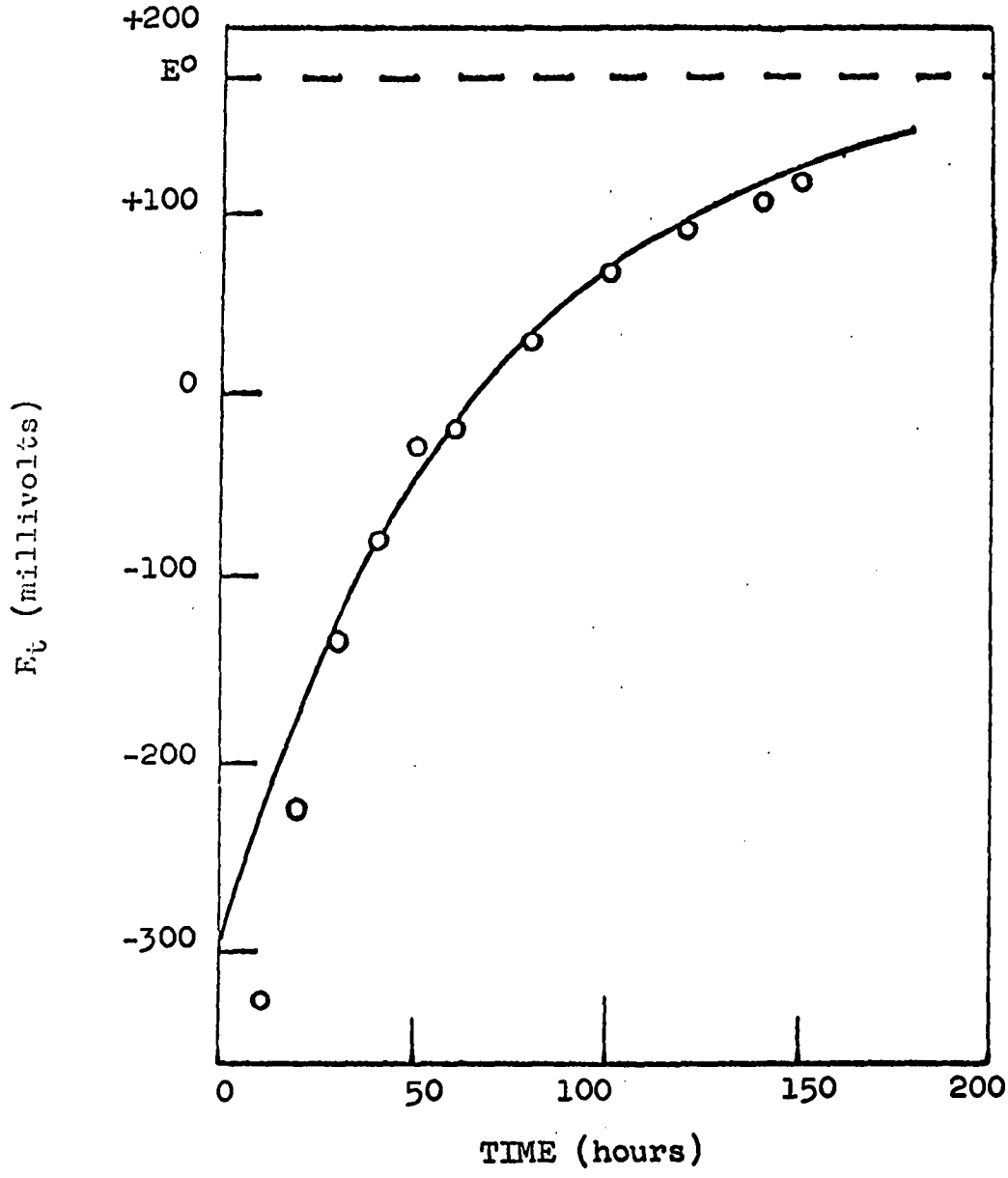


FIGURE 22

E_t vs TIME FOR Ag-1-3

the line is calculated from equation 49, A = -470 millivolts, E^o = +174 millivolts, 1/RC = 0.015 hours^{-1}; the points are experimental

demineralization and concentration cell experiments.

The constant A is a function of the applied potential. It can be calculated theoretically by evaluating equation (47) when t = 0.

$$A = E_{app} - E^{o} \tag{55}$$

where E_{app} is the applied potential. The last two columns of Table 11 show that the agreement between $E_{app} - E^{o}$ and the value for A which fits the experimental data is quite poor. This, together with Figures 18 through 22 shows that the theory does not fit the experimental data during the early part of experiments.

There are several possible explanations for the lack of agreement. The mechanism of electrolyte diffusion from a porous electrode may be different from that of diffusion through a membrane which the theory assumes. This effect may be more pronounced immediately after the external potential is removed, when the concentration difference between the solution within the electrode and the external solution is greatest.

The equations were derived by assuming that the resistance (R) and the capacitance (C) are constant with time. This may not be a very good assumption during the first part of the experiment.

Another assumption was that the concentration was uniform in each compartment. This is probably a good

approximation for the right-hand side of the cell in the model which corresponds, in the actual cell, to the solution compartment through which fresh solution flows constantly. The left-hand compartment of the model cell, however, corresponds to the interior of the electrodes. When the external potential is applied transference process could cause concentration gradients within this compartment or on either side of the membrane.

The presence of these concentration gradients after the applied potential is removed would cause the potential decay curve to be different from that predicted by the simple theory. However after several hours these gradients should be removed by diffusion since the rate of diffusion within a solution compartment is fast compared to diffusion across the membrane. The solution in the left-hand compartment would then be uniform and at a higher concentration than the right-hand compartment and the theory would then be adequate.

Then, the quantity $A + E^{o}$, where A is the constant calculated from the experimental data, would represent the value of the applied potential required to obtain the calculated curve if no concentration gradients existed. The difference between the actual value of E_{app} and $A + E^{o}$ would be the concentration potential resulting from the concentration gradients discussed above.

Capacitance. The capacitance of the condenser in the equivalent-circuit model (see Figure 17b) can be estimated

by considering the work done in charging it. During the charging process the potential difference across its plates increase, corresponding to an increasing concentration gradient in the transference cell (cell 38). The minimum work[35] done in transferring the infinitesimal quantity of electrolyte dy = dQ/F is

$$dW = FEdy = 2RT[\ln(c_1/c_o)]dy \qquad (55)$$

where W is the work and c_1 is the concentration of electrolyte in the left-hand side of the cell. The concentration of electrolyte in the right-hand side of the cell is held constant and is designated by c_o. In this discussion the assumption is made that activities may be replaced with concentrations.

The energy dissipated in R_- of Figure 17b is not included in this calculation. The charge transfer may be imagined to occur infinitesimally slowly, so that there is no energy dissipated in R_+. The charging process is started when $c_1 = c_o$

After y equivalents of electrolyte have been transferred

$$c_1V_1 = c_oV_1 + y \qquad (56)$$

where V_1 is the constant volume of the left-hand compartment of the cell. Equation (56) assumes that transfer of water through the membrane is negligible.

Solving equation (56) for c_1 and substituting into

(55) gives

$$dW = 2RT[\ln(1+y/c_oV_1)]dy \qquad (57)$$

But since $c_oV_1 = n_o$ the original number of equivalents in the left-hand compartment

$$W = \int_o^y 2RT \ln(1+y/n_o)dy \qquad (58)$$

$$W = (2RT/n_o)[(1+y/n_o)\ln(1+y/n_o) - y/n_o] \qquad (58a)$$

when y is small compared to n_o, corresponding to a low applied potential, equation (58) reduces to

$$W = RTy^2/n_o \qquad (59)$$

Equation (59) was derived for the case of an increasing concentration in the left-hand compartment, corresponding to a demineralization (oxidation) cycle. The same result is obtained for a regeneration (reduction) cycle when the left-hand compartment loses electrolyte.

In transporting y equivalents, Fy coulombs are passed through the arm of the circuit containing the condenser. Thus, the work done in charging the condenser, in the region where (59) is valid, is proportional to the square of the charge transferred, a characteristic of a normal condenser.[38]

The capacitance of a normal condenser[38] is $(1/2)Q^2/W = (1/2)F^2y^2/W$ therefore:

$$C = n_o F^2/2RT \qquad (60)$$

Unlike a normal condenser the capacitance is independent of the electrode separation or area. It is a function of the number of moles of electrolyte in the left-hand compartment when $c_1 = c_o$.

Unfortunately n_o cannot be measured. It can be estimated by choosing a reasonable value of the resistance (R) of the cell to internal discharge. Equation (25) shows that the largest resistance is that of the cation membrane to the passage of anions. This would be expected to be rather large, of the order of 10^4 ohms. The product RC can be calculated from Table 11 for the two electrodes. For the electrode used in Experiment Ag-1-1 this product is 1.4×10^5 seconds and is 2.4×10^5 seconds for the electrode used in Ag-1-2 and 3.

The capacitance of the two electrodes is therefore 14 farad and 24 farad respectively if $R = 10^4$ ohms. Then from equation (60) n_o would be 7.5×10^{-6} equivalents and 1.3×10^{-5} equivalents.

The solution used in these two experiments was 0.03 normal. Thus n_o would be 0.03 V, where V is the volume in liters of the left-hand compartment of cell (38) or the volume of solution within the electrodes. This volume would be 0.25 cm^3 for one electrode and 0.45 cm^3 for the other. These values for the internal volume of the electrode seem

quite reasonable. The capacitances are of the same order of magnitude as that calculated by Murphy for a simple transference cell.[35]

Concentration Potential Drifts

The operation of Concentration Cell-2 and the potential drifts encountered have been described in Chapter III. Figure 9 illustrates the typical behavior of these drifts. After electrically conditioning the electrodes and shorting them together with 0.1 N NaCl flowing through the cell only small drifts were observed when the electrodes were unshorted. However, after one electrode had been contacted with 0.01 N NaCl solution and the concentration potential developed a steady decrease in this potential was observed. With both electrodes again in contact with 0.1 N NaCl a bias potential was obtained that was almost equal to the decrease of the concentration potential.

Any successful theory of carbon electrode potentials must explain these drifts. Unfortunately the data available on concentration potential drifts are neither extensive nor accurate enough to warrant a quantitative test of the theory as was done for potential drifts measured against a reference electrode. The phenomenon can be discussed qualitatively in terms of the model proposed for carbon electrodes.

Concentration Cell-2 contained four identical carbon electrodes and an ion-selective membrane. During conditioning one pair of electrodes was oxidized and the other pair

was reduced. The concentration potentials of each pair were then measured as the potential of the cell

$$\underset{\text{electrode (I)}}{\text{carbon}}/\text{NaCl}(a^{I})/\text{M}/\text{NaCl}(a^{II})/\underset{\text{electrode (II)}}{\text{carbon}} \qquad (61)$$

where M represents the ion-selective membrane. The activity of sodium chloride solution in contact with electrode (I) is a^{I} and a^{II} is the activity of solution in contact with electrode (II). Both electrodes are identical and in the same oxidation state. The potential of cell (61) will be designated ΔE.

The potentials of the two cells,

$$\text{Carbon electrode (I)}/\text{NaCl}(a^{I})/\text{Ag-AgCl} \qquad (62)$$

and

$$\text{Carbon electrode (II)}/\text{NaCl}(a^{II})/\text{Ag-AgCl} \qquad (63)$$

which will be designated E_t^I and E_t^{II} respectively, must also be used to discuss concentration potential drifts. These cells are of the same type as cell (37) and both can be represented by the equivalent circuit of Figure 17(b).

The potential drifts of each electrode with respect to the silver-silver chloride electrode can thus be represented by the equivalent circuit method. These potentials (E_t^I and E_t^{II}) will decay according to equation (47). The concentration cell potential, ΔE of cell (61), is given at any time by

$$\Delta E = E_t^{II} - E_t^{I} - t_+ 2RT/F \ln a^I/a^{II} \qquad (64)$$

The last term in equation (64) results from imperfect selectivity of the membrane. It does not contribute to the potential drift and will be ignored in subsequent equations. This is equivalent to assuming that the membrane of the concentration cell is perfectly anion-selective ($t_+ = 0$).

The equivalent-circuit treatment of concentration cell potential drifts must distinguish three separate steps:

Step 1. Both electrodes in contact with 0.1 N NaCl solution

Step 2. Electrode I still contacting 0.1 N NaCl and electrode II in contact with 0.01 N NaCl

Step 3. Both electrodes again contacted by 0.1 N NaCl solution.

The concentration changes associated with electrode II require changes in the equivalent-circuit representation of its potential (E_t) against the silver-silver chloride electrode. Thus at the beginning of Step 2 the potential of the battery in the internal circuit changes from $\mathcal{E}_{0.1} = 2RT/F \ln a_{0.1}$ to $\mathcal{E}_{0.01} = 2RT/F \ln a_{0.01}$ where $a_{0.1}$ and $a_{0.01}$ are the activities of a 0.1 N and 0.01 N sodium chloride solution (see equations 29 and 30). At the beginning of Step 3 the potential of the battery changes back to $\mathcal{E}_{0.1}$.

These changes in the internal circuit cause the

potential of the capacitor (E_c^{II}) to decay at different rates during each of the steps. The decay of potential with time during each step can be obtained by evaluating the constants of equation (41) for the initial conditions, with the time (t) equal to zero, at the beginning of each step. Thus for Step 2, E_c^i the initial potential of the capacitor in equation (41) would be E_c at the end of Step 1 and E_c^i for Step 3 would be E_c at the end of Step 2.

The potential of the concentration cell can be expressed, for any stage, as a function of the constants of equation 41 by combining equations (41), (47) and (64) to give

$$\Delta E_1 = \tau_+[(E_c^i - \mathcal{E})^{II} - (E_c^i - \mathcal{E})^I]\, e^{-t/RC} \qquad (65)$$

During Stage 1, $\mathcal{E}_{0.1}^I = \mathcal{E}_{0.1}^{II}$ and $(E_c^i)^I = (E_c^{i\ II})$, therefore $\Delta E_1 = 0$. Actually if the electrodes were not exactly identical a small, slow, potential drift would be observed. At the end of Stage 1 when $t = t_a$

$$E_c^I = E_c^{II} = (E_c^i - \mathcal{E}_{0.1})\, e^{-t_a/RC} + \mathcal{E}_{0.1} = H \qquad (66)$$

During Stage 2, the time t' will be measured from the end of Stage 1, that is $t' = 0 = t_a$. Therefore $(E_c^i)^I = (E_c^i)^{II} = H$ and

$$\Delta E_2 = \tau_+(\mathcal{E}_{0.01}^{II} - \mathcal{E}_{0.1}^I)e^{-t'/RC} \qquad (67)$$

$$\Delta E_2 = -\tau_+(2RT/F)(\ln a_{0.1}/a_{0.01})e^{-t'/RC} \qquad (67a)$$

Therefore the concentration cell gives the true concentration potential at the beginning of Stage 2, when $t' = 0$. The potential then decays slowly toward zero. If $t' = t_b'$ at the end of Stage 2 the difference between E_2 at $t' = 0$ and $t' = t_b$ is

$$E(\text{bias}) = -\tau_+(2RT/F)(\ln a_{0.1}/a_{0.01})(1 - e^{-t_b'/RC}) \qquad (68)$$

If the potentials of the capacitors in the internal circuits at the end of Step 2 are

$$E_c^I = (H - \mathcal{E}_{0.1}^I)\, e^{-t_b'/RC} + \mathcal{E}_{0.1}^I = I \qquad (69)$$

and

$$E^{II} = (H - \mathcal{E}_{0.01}^{II})\, e^{-t_b'/RC} + \mathcal{E}_{0.01}^{II} = J \qquad (69a)$$

then the concentration cell potential during Step 3 is

$$\Delta E_3 = \tau_+(J - I)\, e^{-t''/RC} \qquad (70)$$

$$\Delta E_3 = \tau_+(\mathcal{E}_{0.01}^{II} - \mathcal{E}_{0.1}^I)(1 - e^{-t_b'/RC})\, e^{-t''/RC} \qquad (70a)$$

$$\Delta E_3 = -\tau_+(2RT/F)(\ln a_{0.1}/a_{0.01})(1 - e^{-t_b'/RC})\, e^{-t''/RC} \qquad (70b)$$

At the beginning of Step 3, when $t'' = 0 = t_b'$ the potential is equal to the bias developed at the end of Step 2 (equation 68) from the potential drift. This potential also

slowly decays toward zero with time.

The equivalent-circuit model therefore agrees qualitatively with the observed behavior of the concentration potential drifts. The potential drifts during concentration cell experiments seem to be caused by the same mechanism as the potential decay after conditioning; that is, the diffusion of electrolyte into or out of the electrodes. The rate of diffusion and therefore potential decay is a function of the salt concentration of the solution contacting the electrode.

When both electrodes are in contact with the same solution the rate of potential decay is the same and the potential difference between the two is zero. Changing the solution in one electrode develops the concentration potential but also changes the rate of potential decay of one electrode. The difference in decay rate causes a bias potential to develop between the two electrodes. This bias is observed when both electrodes are again contacted by the same solution causing the concentration potential to go to zero. The bias then decays because the solutions are the same on both sides.

CHAPTER V

SUMMARY AND CONCLUSIONS

The concentration cell method has been established as a reliable means of characterizing carbon electrodes. The use of this method led to the development of predominantly anion-responsive electrodes based on carbon.

Concentration cell experiments revealed that all the carbon electrodes studied were partially responsive to both cations and anions. The relative responsiveness to each ion type was expressed by an electrode selectivity coefficient $\mathcal{T}$, which is analogous to the selectivity coefficients used to characterize membranes.

While demineralization cell behavior is outside the scope of this study, some of the results of this work can be applied in this area. Electrode selectivity coefficients are one example. The fact that the electrodes are not completely responsive to one ion type will contribute to loss of current efficiency. It would also be interesting to determine the selectivity coefficients of electrodes to other than sodium and chloride ions.

All of the factors that influence ion selectivity and

capacity of carbon electrodes were not determined. This type of information cannot be obtained from potential measurements alone. The most important factor in determining selectivity seems to be the nature of the dispersing agent used in preparing an electrode. In general cationic polyelectrolytes used as dispersants give predominantly anion-responsive electrodes while cation-responsive electrodes are obtained with anionic dispersants. Electrochemically active additives were found to have little or no effect on capacity of the electrodes. They did seem to influence the selectivity to some degree. No definite conclusions could be drawn about the influence of different types of carbon or the presence of surface oxide groups.

The potential of electrically conditioned carbon electrodes were measured with respect to reference electrodes such as silver-silver chloride. These potentials were found to decay slowly with time over a period of several days.

These potential decays were explained with a model of carbon electrodes that represents them as a combination of a perfect electrode and an imperfect ion-selective membrane. The selectivity coefficient of the membrane represents the selectivity ($\mathcal{T}$) of the electrode. This model is consistent with the proposal by Smith[27] that the polyelectrolytes used as dispersants may dry and form a film over the carbon surface that acts as an ion-selective membrane.

The model of carbon electrodes was treated by an

extension of the equivalent circuit model of transference cells proposed by Murphy.[35] The equation derived from this model fits the experimental data quite well except for the first few hours after the conditioning potential was removed. The lack of fit in this region was attributed to concentration polarization at the electrode solution interface and within the electrode itself, induced by the conditioning current.

The equation contained three constants; the constant A was related to the initial potential (that applied during conditioning, the final potential of the cell E^{o} which is a function of the nature of the carbon and reference electrodes, and the constant 1/RC where R and C are parameters of the equivalent circuit model.

The internal resistance of the equivalent circuit is represented by R. It includes the sum of the resistances of both the solution and the membrane to cations and anions. The constant C represents the capacitance of the capacitor in the equivalent circuit. This constant was related to the number of equivalents of electrolyte within the electrode when the internal solution is in concentration equilibrium with the solution external to the electrode. Neither R nor C can be measured directly. Estimates of these constants were made which agree with the measured values of 1/RC.

The other two constants can be measured directly. If the decay is studied over a long enough time the potential

should level off at E^{o}. The experimental data that were available did not extend to long enough times and E^{o} was calculated by the method of Guggenheim.[39] The lack of agreement between the theory and data in the early part of the experiment caused considerable difference between the actual applied potential and that calculated from the theory. This could probably be minimized by conditioning at lower voltages.

The equivalent-circuit model was used to explain the potential drifts observed during concentration cell experiments. The theory predicts that concentration potentials should drift in the manner observed but the data available were not accurate enough to warrant a quantitative test of the theory. Such data would be difficult to obtain since both electrodes are drifting throughout the course of the experiment. It might be possible in a cell which could measure the potentials of both carbon electrodes against a silver-silver chloride electrode and the concentration cell potential simultaneously.

The equivalent-circuit model could probably be applied to demineralization cell experiments. In fact any further tests of the theory should probably be in this area.

Demineralization data currently available support the physical basis of the model as a combination of an electrode and an ion-selective membrane. Rather large pH changes have been observed[37] in demineralization cell experiments. With predominantly cation-responsive electrodes the pH drops

during the regeneration cycle and increases during demineralization. This is consistent with pH changes observed in cells containing electrodes and ion-selective membranes.[40]

APPENDIX I

EXPERIMENT CODE DESIGNATIONS

A complete code designation identified which concentration cell was used by beginning with CC-1 or CC-2. Each experiment was then numbered consecutively using a different series for each cell.

For example: CC-1-22 would be the twenty second experiment with concentration cell 1.

This designation is followed by the electrode identification code (see Appendix III) and designations giving the normality of the solutions and the type of membrane.

For example: CC-2-1 (A/0.1 N NaCl/A_M/0.01 N NaCl/A) would be the first experiment with CC-2 using a pair of Aquadag electrodes (A) with 0.1 N sodium chloride in one compartment and 0.01 N sodium chloride in the other with an anion-permeable membrane separating the two halves of the cell.

The full experiment code was not used in all cases. Abbreviated forms of the code were used when there seemed no chance of confusion.

APPENDIX II

ELECTROCHEMICAL SIGN CONVENTION

In keeping with standard usage of American electrochemists the sign of a cell potential was taken as positive if the left-hand electrode of the cell as written was the negative electrode or anode. If the left-hand electrode was positive the cell was given a negative potential.

The sign of concentration cell potentials was determined on the basis of the left-hand compartment containing the more concentrated solution. Thus the left-hand electrode of the cell:

C/0.1 N NaCl/A_M/0.01 N NaCl/C

(where C is an cation-responsive electrode and A_M an anion-permeable membrane) was positive and the sign of the cell potential was negative.

APPENDIX III

ELECTRODE CODE DESIGNATIONS

The electrodes are identified by a series of letters. The first letter denotes the type carbon used. If the carbon received any type of chemical treatment this is indicated by a series of letters in parentheses. If a dispersing agent was used this is identified by a series of letters separated from the rest of the code by dashes. If chemical additives were used they are designated by a series of letters separated by dashes.

The code designations are:

Type of Material	Code Letter(s)	Name
Carbons	A	Aquadag
	D	Dixon's Air Spun Graphite
	N	Norite
Chemical Treatments	MA	Mixed Acid
	OT	Oleum treatment
Dispersants	TA	Tannic acid
	PSA	Polystyrene sulfonic acid
	PVII	Polyvinylimidazol quaternized with methyl iodide

(Code designations Continued)

Type of Material	Code Letter(s)	Name
	PVIS	Polyvinylimidazole quaternized with methyl sulfate
Additives	TMPD	Tetramethylphenylene-diamine
	TMB	Tetramethylbenzidine
	QS	Quaternized safronine
	DMPD	Dimethylphenylenediamine

Aquadag contained its own dispersant and therefore an electrode prepared from it, with no additives used, could be designated by the single letter A. Other electrodes require more letters:

Examples

Code	Electrode
A(OT)-TA	oleum treated Aquadag dispersed with tannic acid
N-PVII	Norite dispersed with polyvinylimidazolemethiodide
N-PVII-TMB	same as above with TMB added

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